An aerial photograph of a city skyline, likely Atlanta, Georgia, viewed from a distance. The foreground is dominated by a dense, dark green forest. The city buildings are silhouetted against a hazy, light-colored sky. The overall scene is atmospheric and somewhat muted in color.

**The role of nitrate radicals (NO_3) in aerosol life cycle:
Secondary organic aerosol formation and aging of atmospheric
organic aerosols**

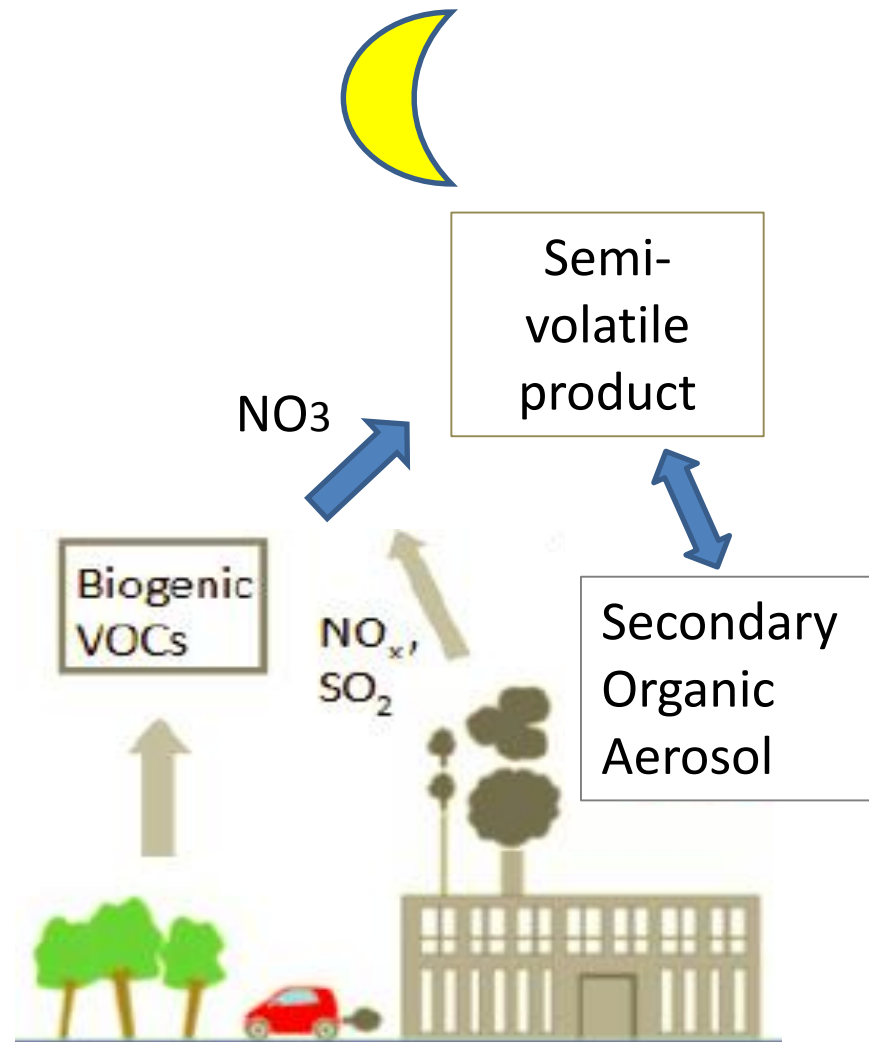
**Nga Lee “Sally” Ng,
Lu Xu, Christopher Boyd, Theodora Nah, Javier Sanchez
Georgia Institute of Technology**

+ SOAS collaborators

**EPA STAR Review
March 14, 2016**

Nitrate Radical Oxidation of BVOCs

- Nitrate radicals (NO_3) are a major night time oxidant
 - Reacts with approximately 20% of all biogenic volatile organic carbons (Pye et al., 2010)
- Monoterpene+ NO_3 reaction has high organic nitrate and SOA yields (e.g., Griffin et al., 1999; Fry et al., 2009)
- NO_3 is created by the reaction of anthropogenic NO_2 with O_3



Nitrate radical oxidation of BVOCs represent a direct way for linking anthropogenic emissions and biogenic SOA formation

Synergetic Approach of Studying Organic Aerosols

Research Goal: determine the extent to which NO_3 radicals oxidation of BVOC affect organic aerosol loading and composition over its atmospheric lifetime

Foundation for predicting
aerosol formation

Laboratory
studies



Evolution of ambient aerosols
(sources, processes, fates)

Field
measurements



Instrumentation

Advanced mass spectrometry

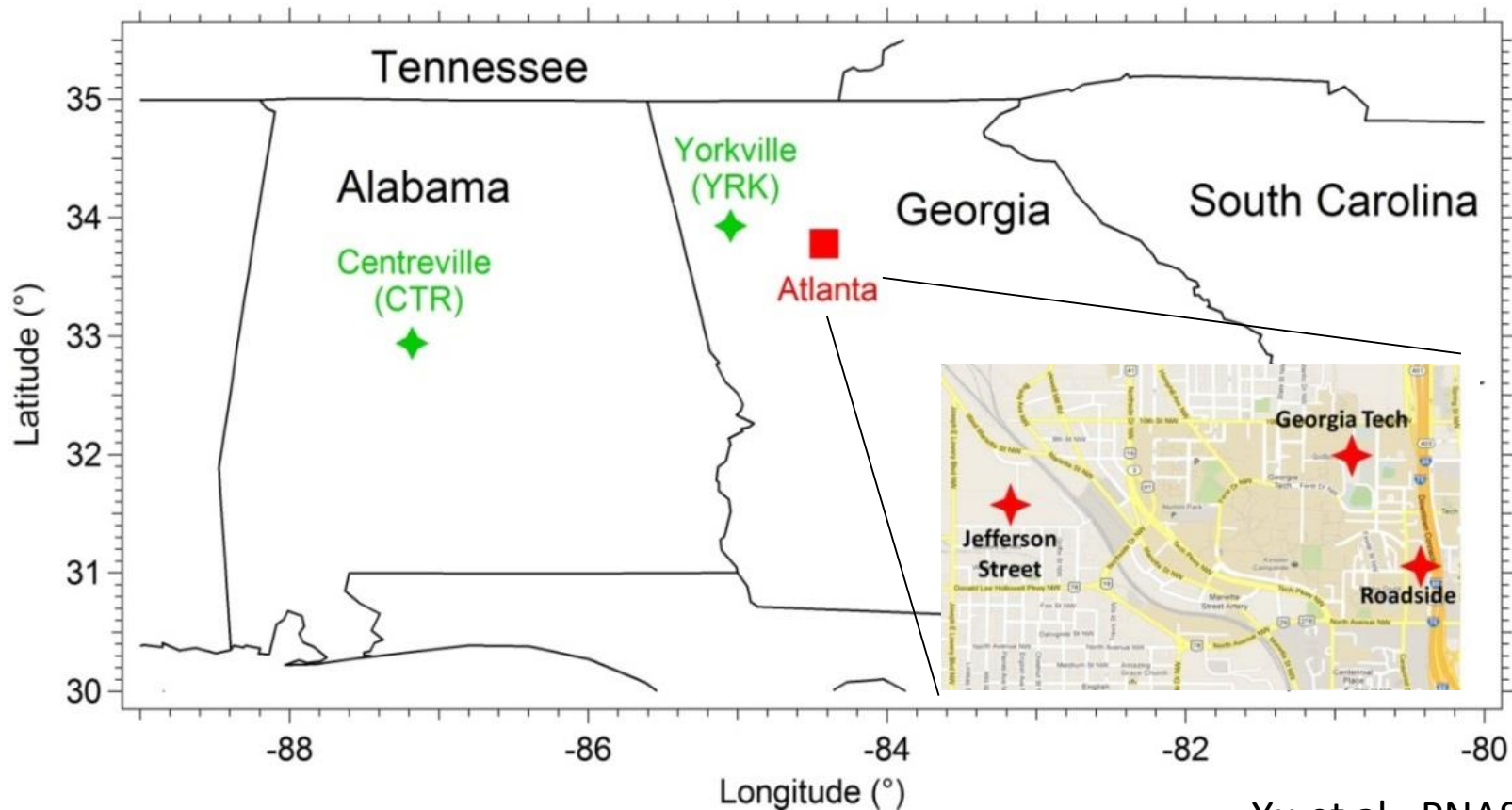
Field Measurements: SOAS and SCAPE

❖ Southern Oxidant and Aerosol Study (SOAS)

- 2013 June - July
- Centreville (rural Alabama)

❖ Southeastern Center of Air Pollution and Epidemiology study (SCAPE)

- 2012 May - 2013 Feb
- Greater Atlanta Area (urban and rural)

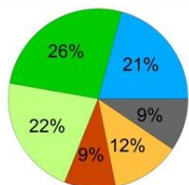


Xu et al., PNAS, 2015

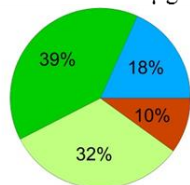
Xu et al., ACP, 2015

OA Source Apportionment in the SE US

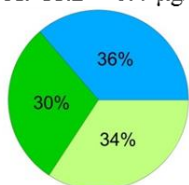
Jefferson Street (May)
OA: $9.1 \pm 4.3 \mu\text{g}/\text{m}^3$



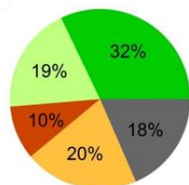
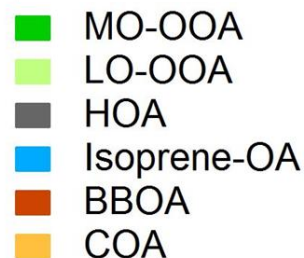
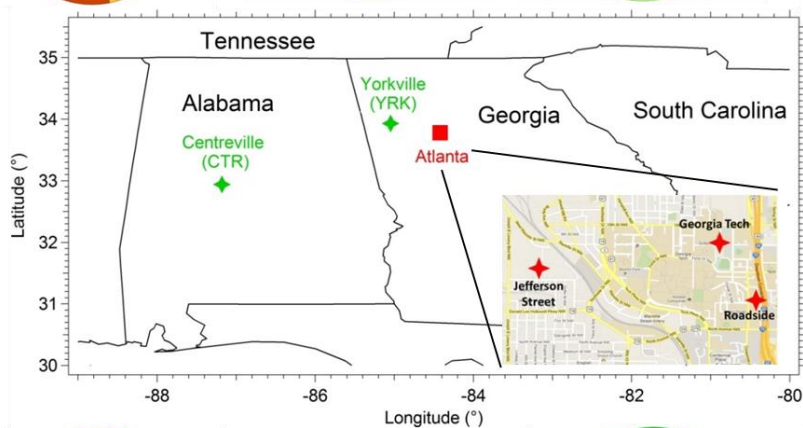
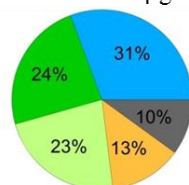
Centreville (June)
OA: $5.0 \pm 4.0 \mu\text{g}/\text{m}^3$



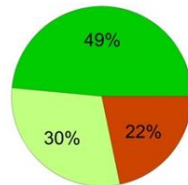
Yorkville (July)
OA: $11.2 \pm 6.4 \mu\text{g}/\text{m}^3$



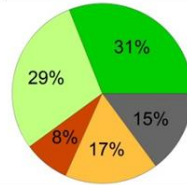
Georgia Tech (Aug)
OA: $9.6 \pm 4.4 \mu\text{g}/\text{m}^3$



Jefferson Street (Nov)
OA: $7.9 \pm 5.1 \mu\text{g}/\text{m}^3$



Yorkville (Dec)
OA: $3.2 \pm 2.3 \mu\text{g}/\text{m}^3$

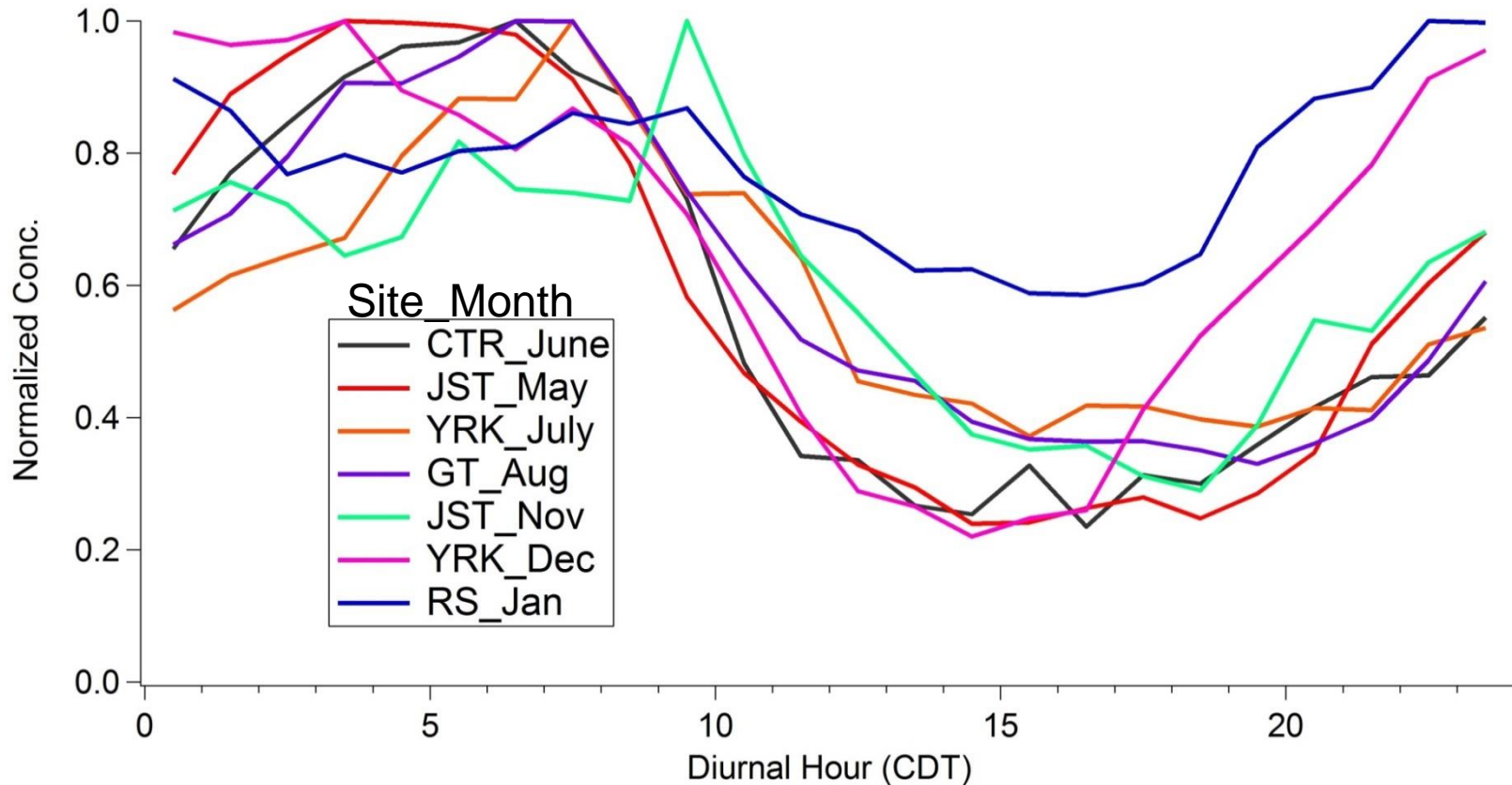


Roadside (Jan)
OA: $4.7 \pm 3.6 \mu\text{g}/\text{m}^3$

- OA sources vary spatially and seasonally
- **Less-Oxidized Oxygenated Organic Aerosol (LO-OOA)** is an important factor across all seasons and sites
- LO-OOA can account for 19-34% of total OA in SE US

Xu et al., PNAS, 2015

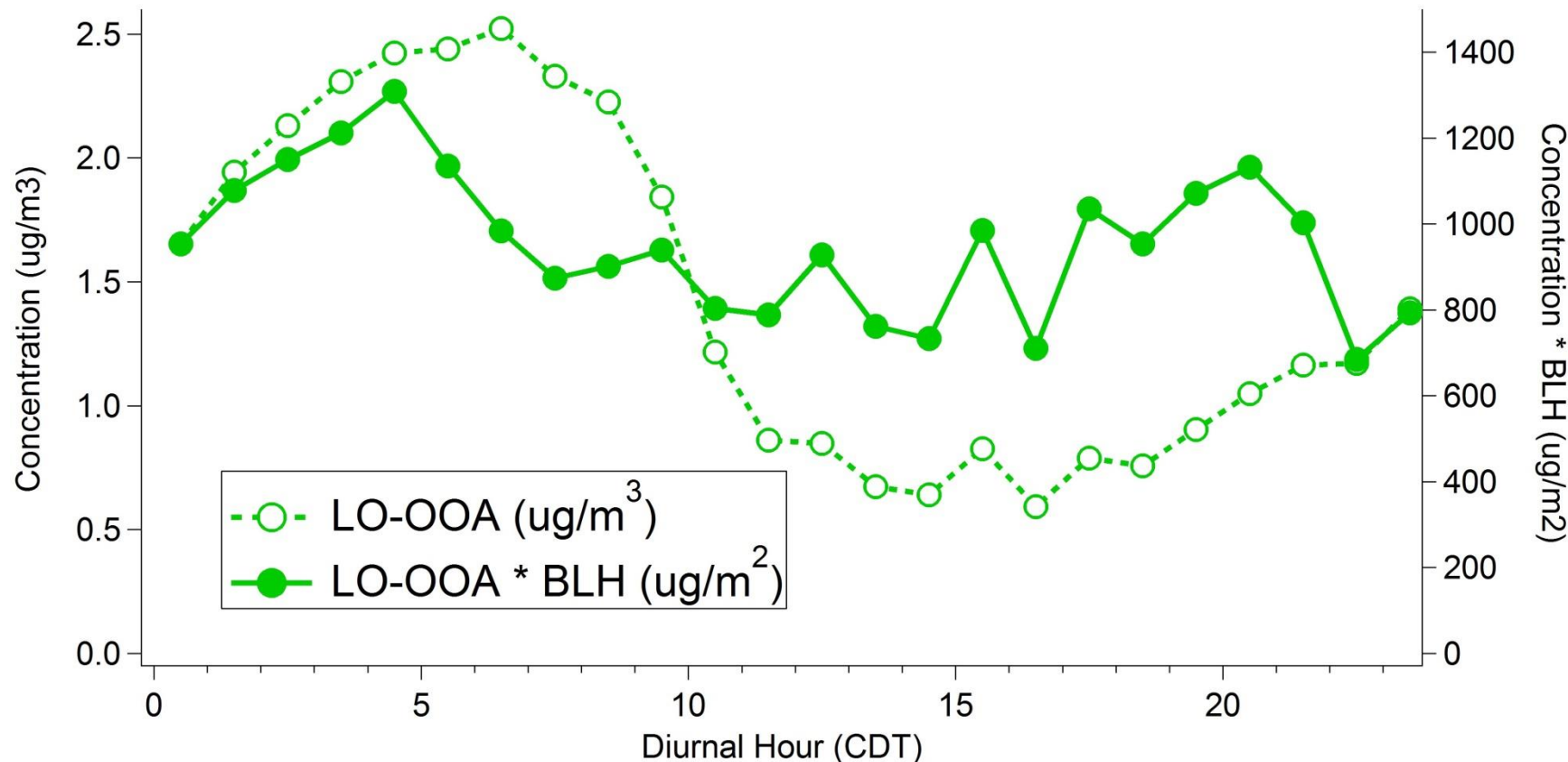
LO-OOA Source: local production or long-range transport?



- Diurnal trends are similar for all sites and all seasons (diurnal trends are normalized by the highest LO-OOA concentration of each dataset).
- A diurnal maximum at night and a minimum in the afternoon.

LO-OOA Nighttime Increase

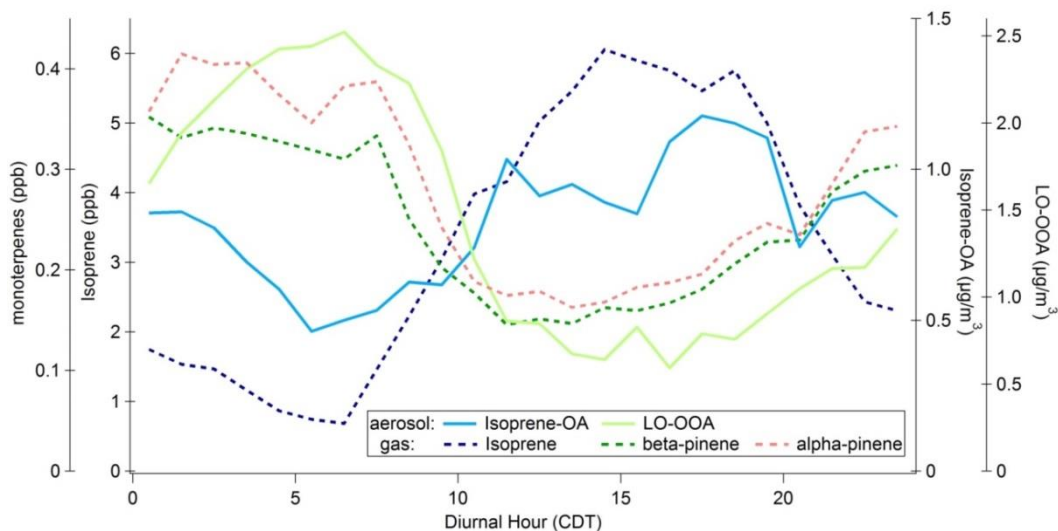
-- boundary layer height change or production?



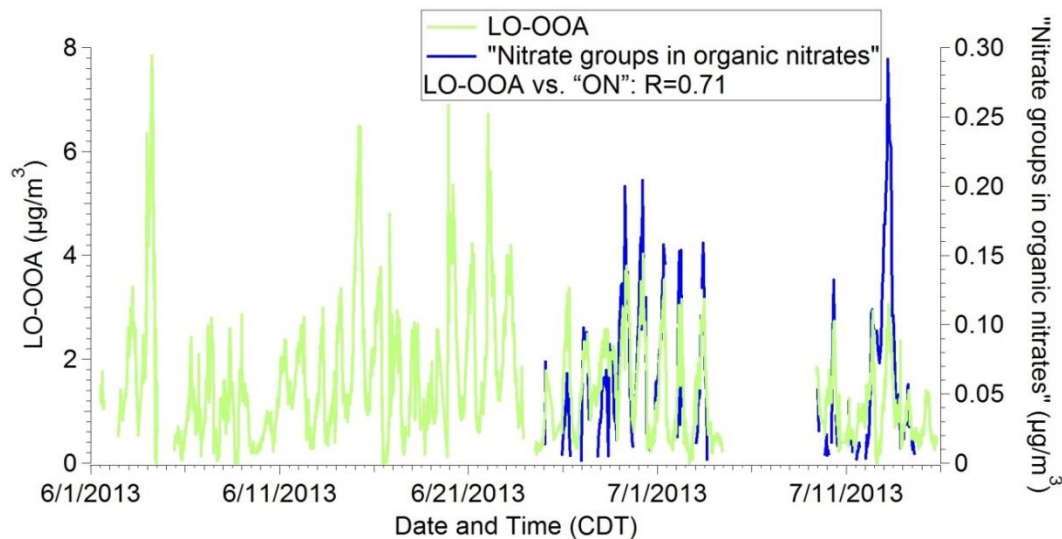
Nighttime increase still exists after adjusting by the boundary layer height

→ nighttime aerosol production

LO-OOA at SOAS



- LO-OOA peaks at night and has same diurnal as monoterpenes.
- LO-OOA is identified in all seasons → monoterpene seasonal variation



- LO-OOA is strongly correlated with "nitrate groups (-ONO₂) in organic nitrates"
- Estimated based on AMS-IC method

Contribution of monoterpenes + NO₃[•] chemistry to LO-OOA

Estimation of Particulate Organic Nitrates

Three independent methods to estimate particulate organic nitrates

1. AMS-IC method: AMS total nitrate - PILS inorganic nitrate

2. AMS $\text{NO}^+/\text{NO}_2^+$ ratio method: (Farmer et al., 2010)

$\text{NO}^+/\text{NO}_2^+$ of ambient OA

$$\text{NO}_{2,\text{org}} = \frac{\text{NO}_{2,\text{meas}} \times (R_{\text{meas}} - R_{\text{AN}})}{R_{\text{ON}} - R_{\text{AN}}}$$

$\text{NO}^+/\text{NO}_2^+$ for ammonium nitrate
(~ 2)

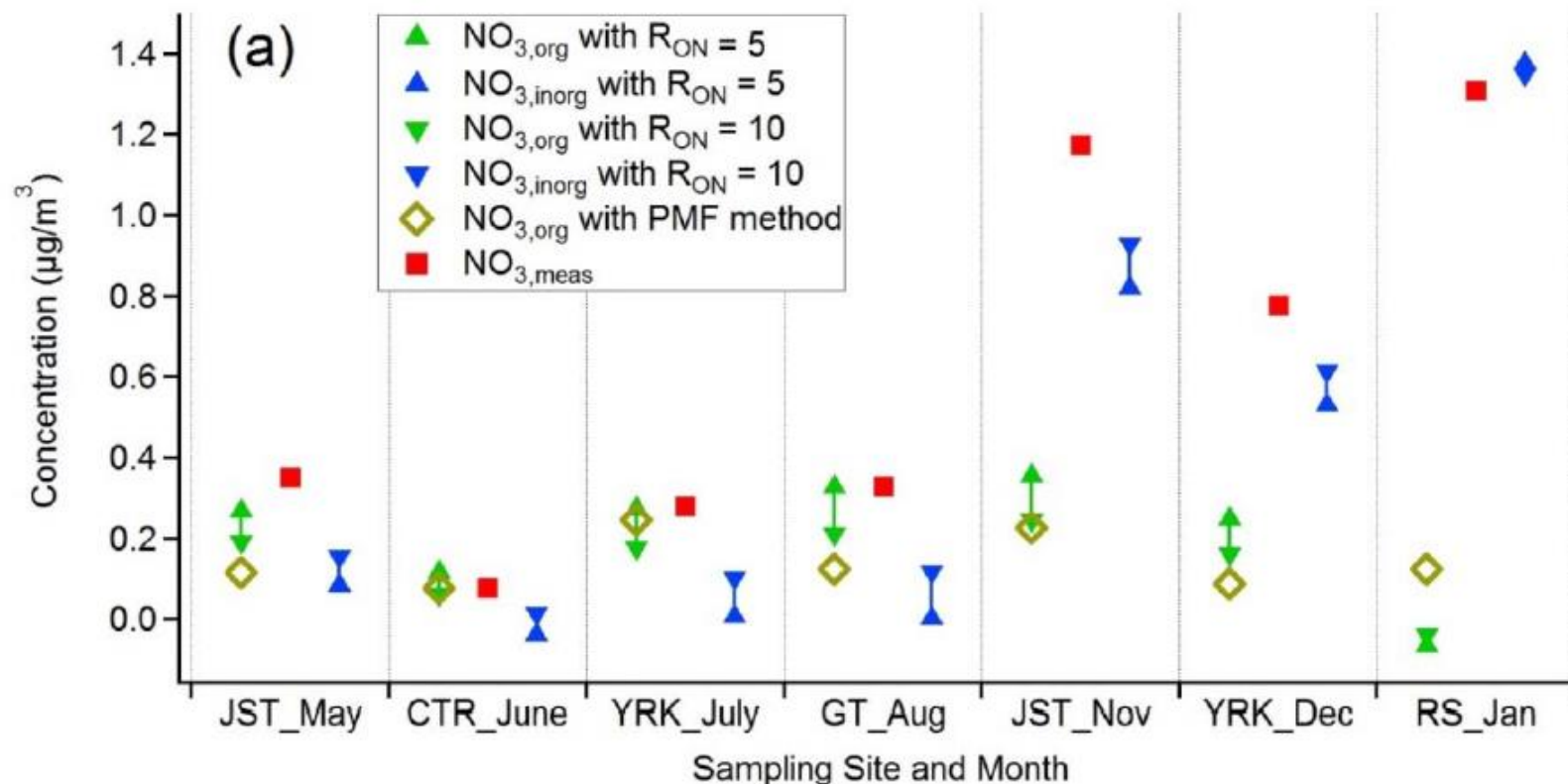
$$\text{NO}_{\text{org}} = R_{\text{ON}} \times \text{NO}_{2,\text{org}}$$

$\text{NO}^+/\text{NO}_2^+$ for organic nitrate
(depends on VOC, instrument, etc, ~ 5 -10)

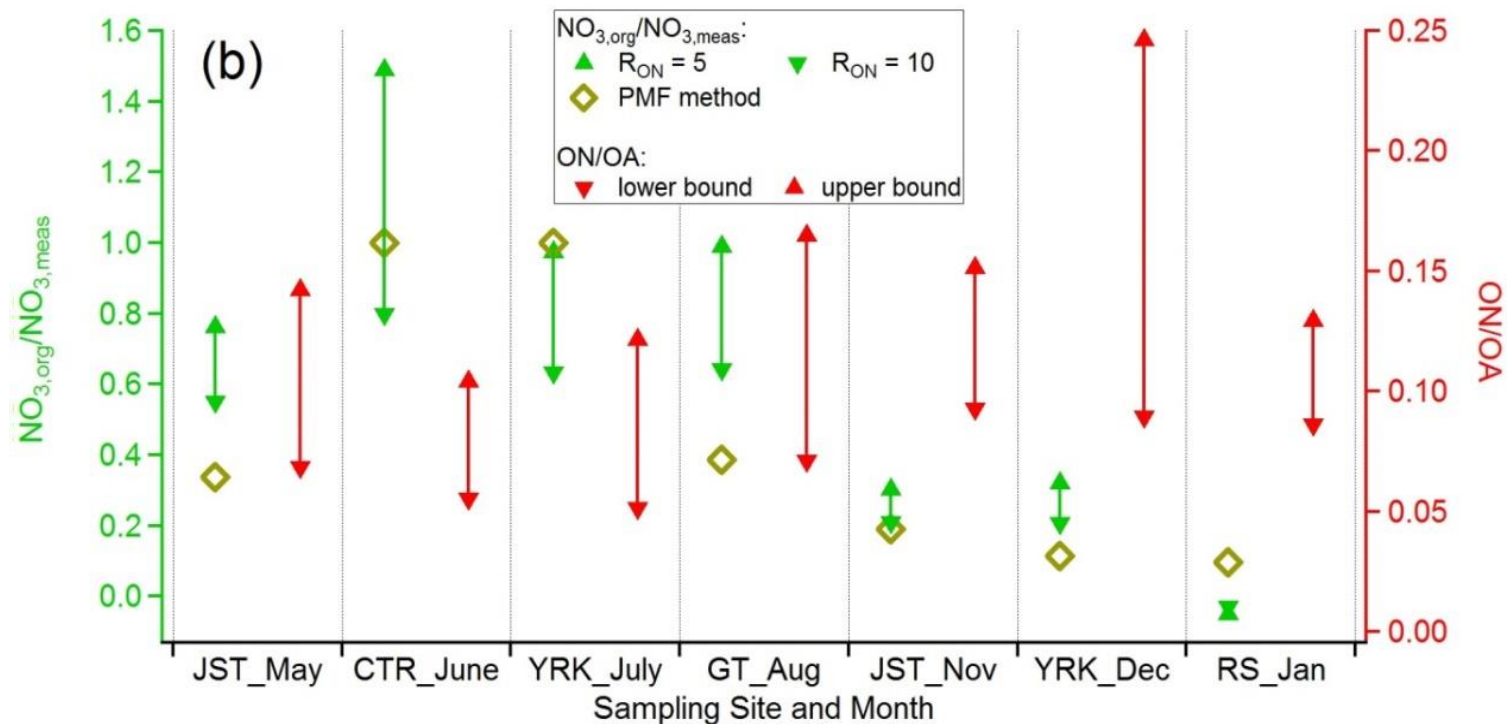
3. PMF method: include NO^+ and NO_2^+ in PMF analysis

NO_3_{org} and $\text{NO}_3_{\text{inorg}}$ in the SE US

- Concentration of “nitrate groups” (-ONO₂)
- **Organic origin:** similar amount year round, is $\sim 0.2 \text{ ug/m}^3$
- **Inorganic origin:** higher in winter months, $\sim 0.8 - 1.4 \text{ ug/m}^3$



Ubiquitous Presence of Particulate Organic Nitrate



Organic origin: 63-100% of total “nitrate groups” conc. in summer

**Organic nitrates are 5-12% of total OA in summer
(assume MW = 200 -300 g/mole)**

Xu et al., ACP, 2015

Fundamental Lab Studies: Monoterpenes + NO₃

1. Laboratory studies of SOA formation from monoterpenes + NO₃ SOA (SOA yields, formation mechanisms, organic nitrates)

- Effect of RH
- Seed Acidity (highly acidic seed, Guo et al., 2015)
- Peroxy radical fate: Mostly likely “Low-NO_x” chemistry (RO₂+HO₂)
- Loadings ~ 10 μg/m³
- α-pinene, β-pinene, limonene

2. Changes in SOA and organic nitrates with continued processing

- Hydrolysis
- Dilution
- Temperature Change
- Dark/photochemical aging

Fate of Peroxy Radicals (RO₂)

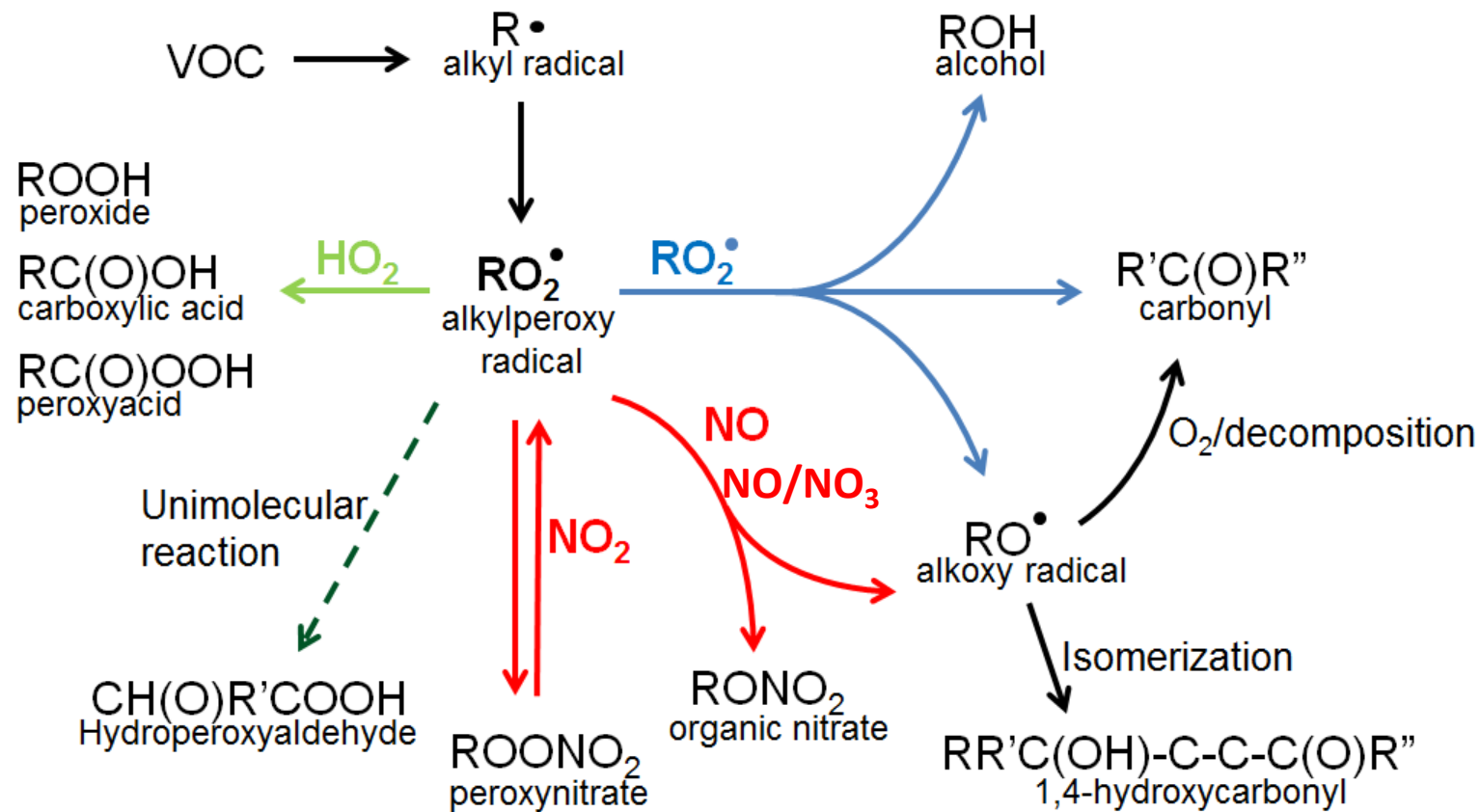
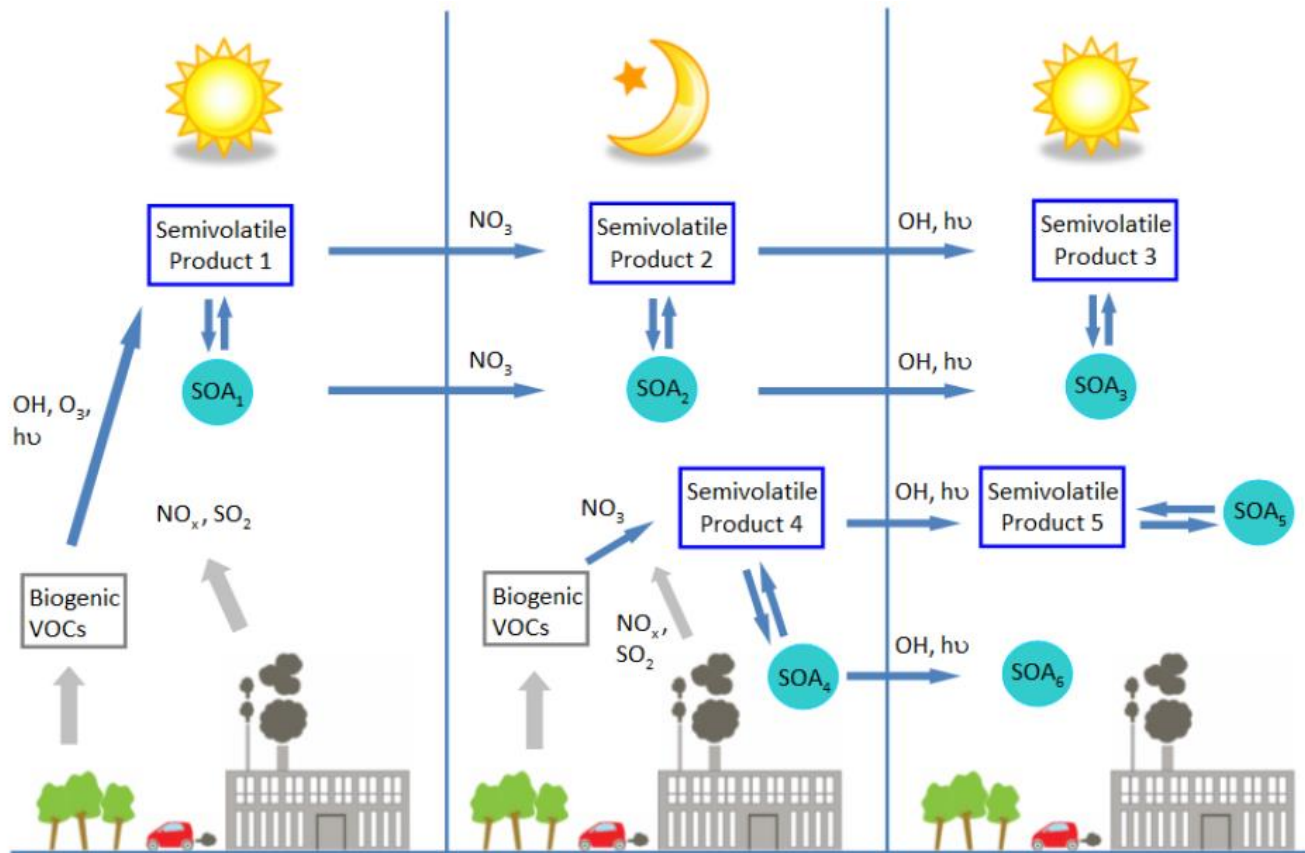


Figure 1. General schematic of gas-phase peroxy radical chemistry in SOA formation.

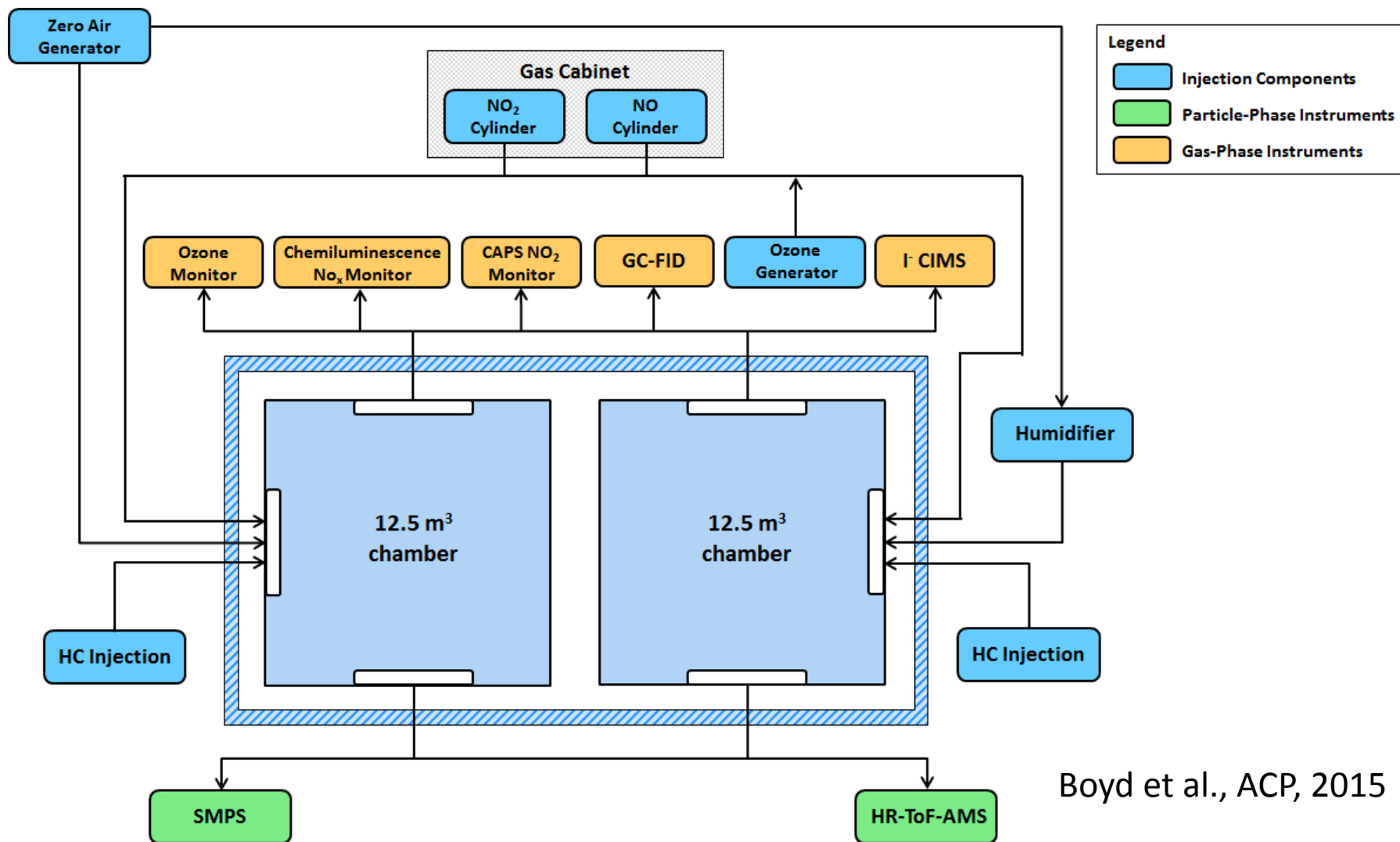
Continued Processing of OA and ON

- Different Perturbations
- Changes with hydrolysis, atmospheric dilution, temperature change, photochemical (OH) and dark (NO₃) aging,



Georgia Tech Environmental Chamber Facility

Dual chamber facility, 300 lights, temperature range 4- 40 °C.



Boyd et al., ACP, 2015

Georgia Tech Environmental Chamber Facility



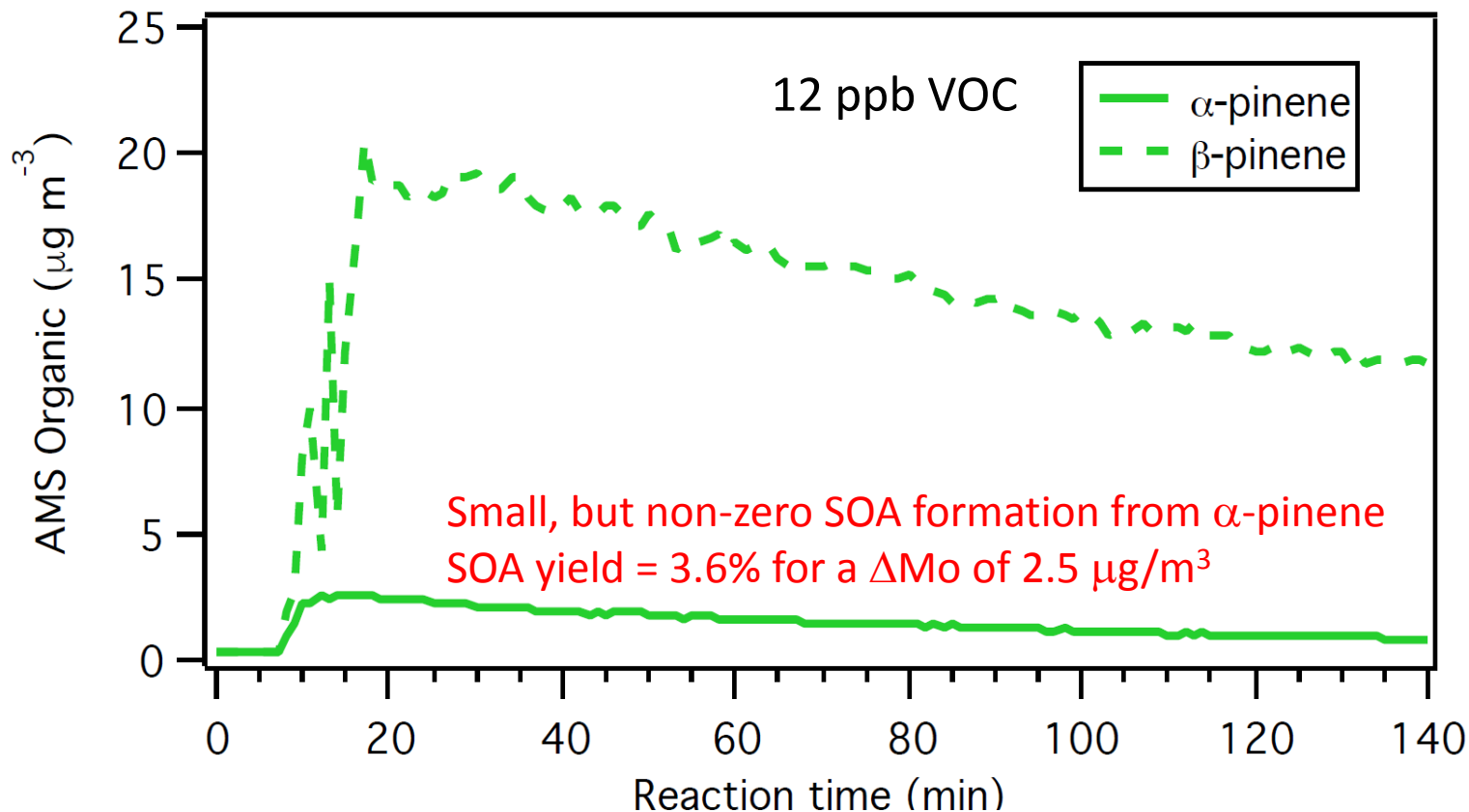
Gas-phase measurements

- Q-CIMS
- HR-ToF-CIMS
- GC-FID
- O₃ monitor
- Chemiluminescence NO/NO₂/NO_x analyzer
- CAPS NO₂ monitor

Particle-phase measurements

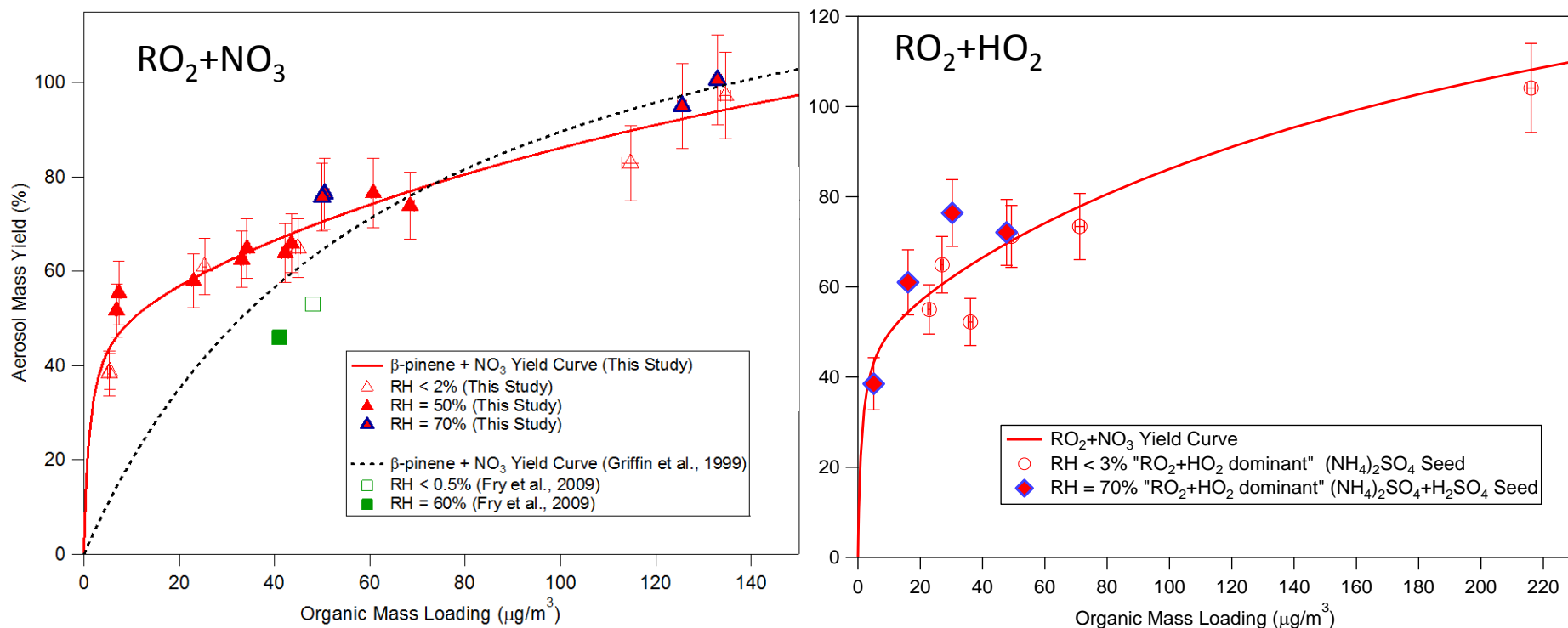
- HR-ToF-AMS
- FIGAERO-HR-ToF-CIMS
- SMPS
- CPC
- Offline filter characterization

SOA Formation from α -pinene + NO_3 and β -pinene + NO_3



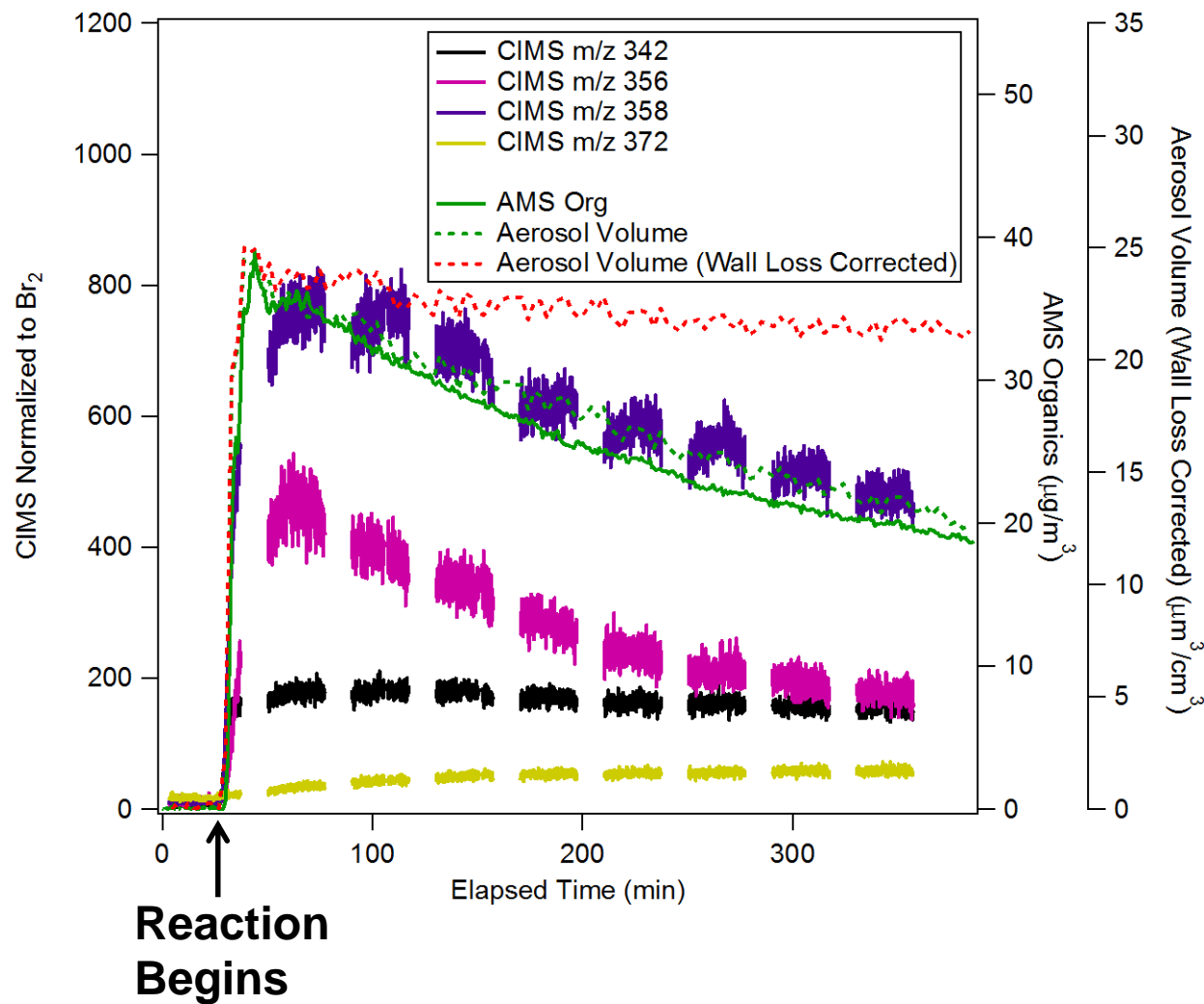
- Temperature = 25 °C
- RH = 50 – 54%
- Highly acidic $\text{MgSO}_4/\text{H}_2\text{SO}_4$ seed
- RO_2+HO_2 and RO_2+NO_3 pathways

β -pinene+NO₃: SOA Yields



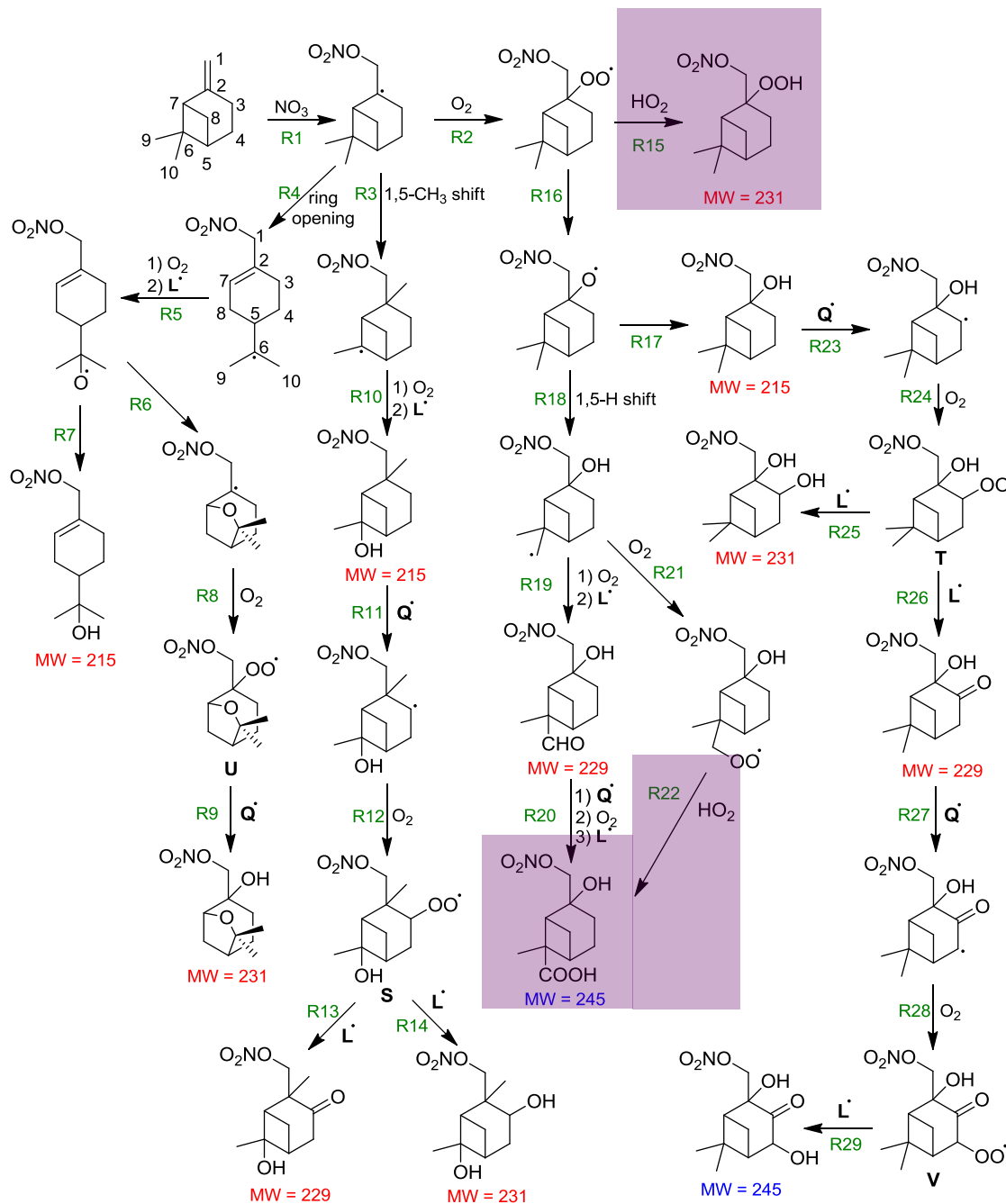
- Humidity and RO₂ fate does not have a strong effect on aerosol mass yield
- Aerosol mass yields: 27.0-104.1% for mass loadings ranging from 5.1-216.1 $\mu\text{g}/\text{m}^3$
- **β -pinene+NO₃ can potentially contribute to a large fraction of ambient aerosol**

β -pinene+NO₃ : Gas-phase Products



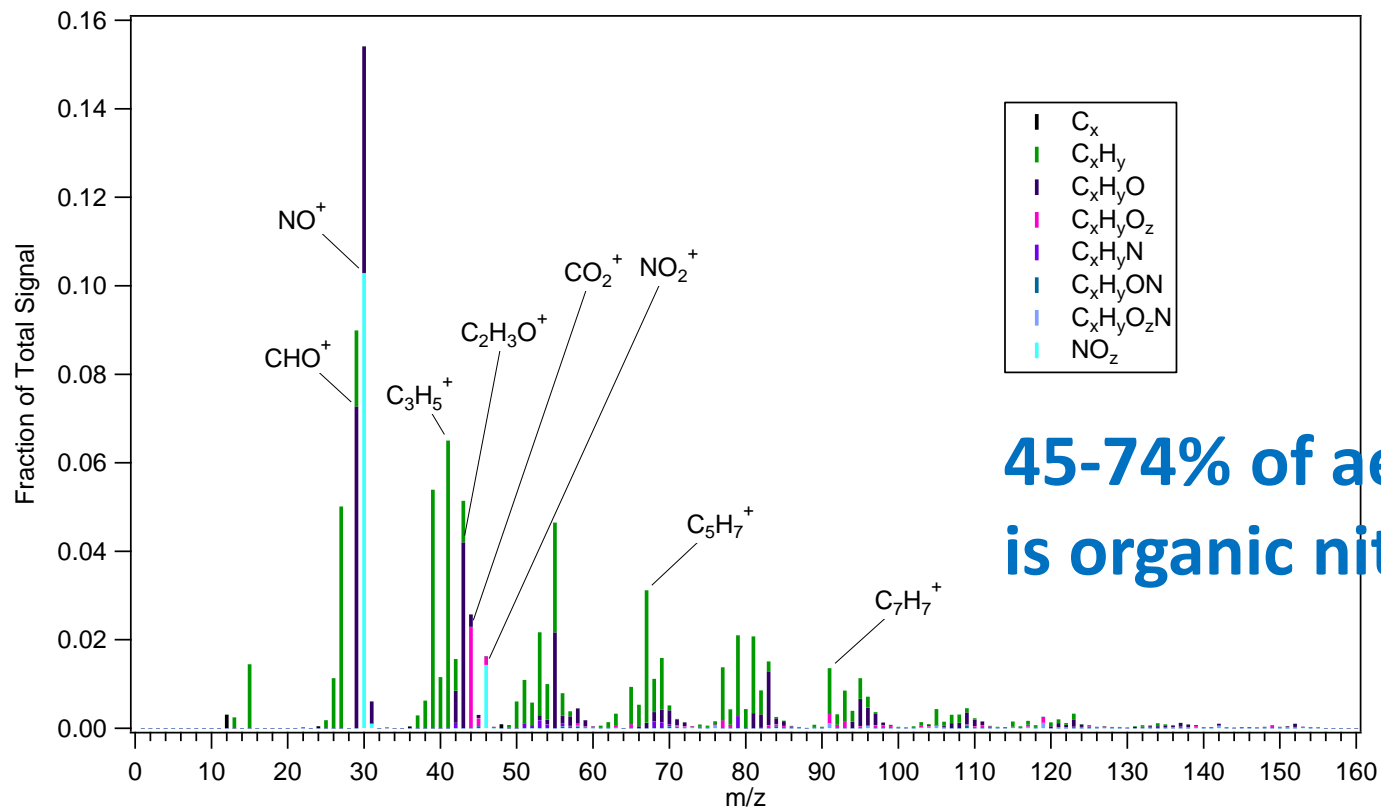
- Aerosol and gas phase species appear almost immediately
- Organic nitrate species identified by Q-CIMS
- Fast reaction with immediate condensation of products

Boyd et al., ACP, 2015



Molecular weight (g/mol)	Chemical Formula	Vapor Pressure @293K (atm)
215	$\text{C}_{10}\text{H}_{17}\text{NO}_4$	$8.5 \cdot 10^{-8}$
229	$\text{C}_{10}\text{H}_{15}\text{NO}_4$	$3.8 \cdot 10^{-9}$
231	$\text{C}_{10}\text{H}_{17}\text{NO}_5$	$4.8 \cdot 10^{-8}$
231	$\text{C}_{10}\text{H}_{17}\text{NO}_5$	$5.0 \cdot 10^{-10}$
245	$\text{C}_{10}\text{H}_{15}\text{NO}_6$	$2.2 \cdot 10^{-11}$
245	$\text{C}_{10}\text{H}_{15}\text{NO}_6$	$5.8 \cdot 10^{-11}$

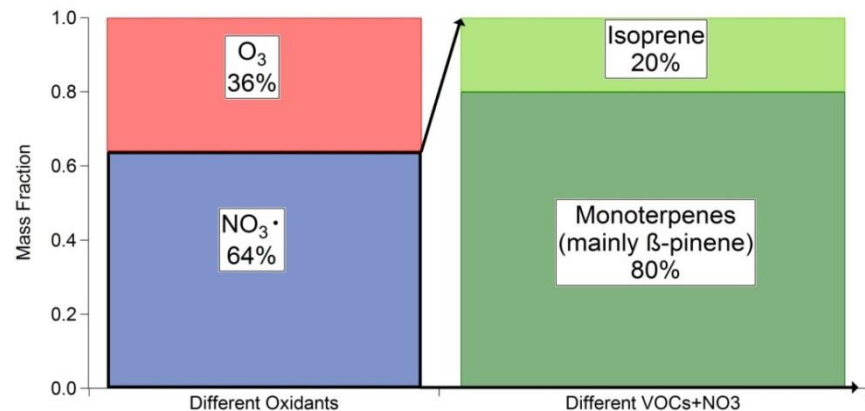
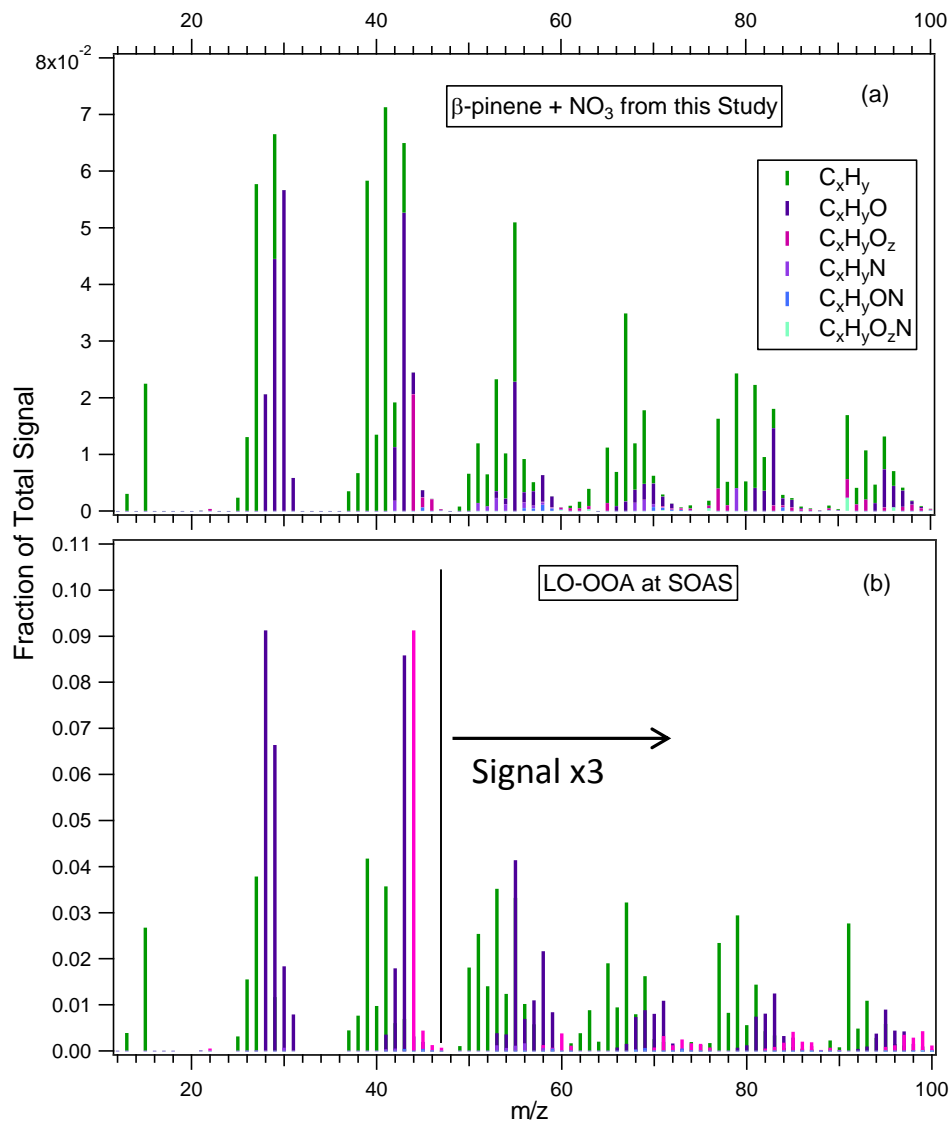
β -pinene+NO₃: Aerosol Composition and Dark Aging



- Large fraction of nitrate species at NO⁺ (m/z 30) and NO₂⁺ (m/z 46), 11%
- NO⁺ / NO₂⁺ ratio = 4.8 – 10.2
- Relatively large signal at m/z 67 (C₅H₇⁺) and m/z 91 (C₇H₇⁺)
- Increase in O/C with dark aging: 18% (dry), 6% (humid)

Relevance of β -pinene+NO₃ to SOAS

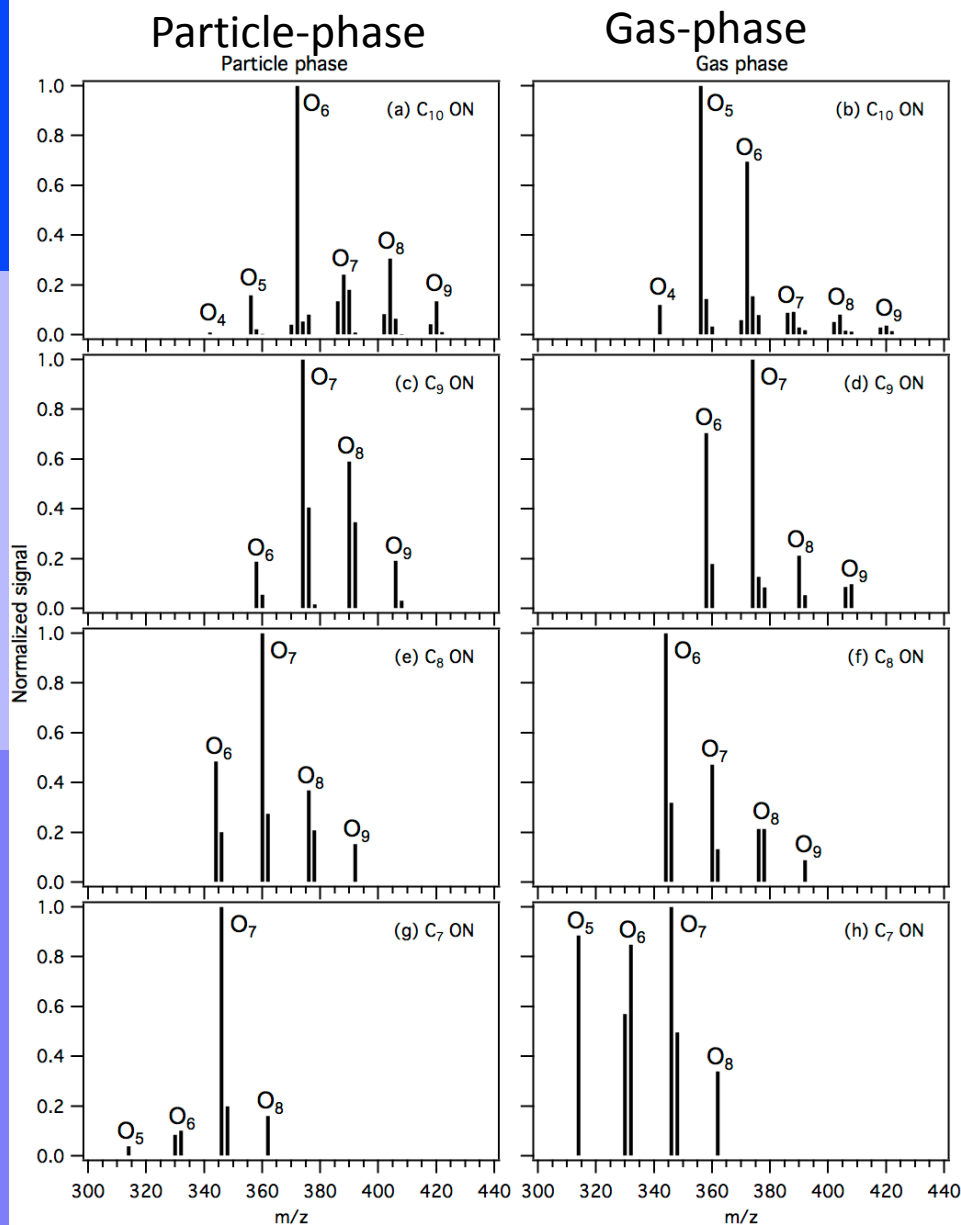
Spectrum of LO-OOA at SOAS has similar features to laboratory β -pinene+NO₃ SOA at $m/z > 60$



Using results from chamber experiments →

β -pinene+NO₃ can potentially make up as much as 50% of nighttime OA production at SOAS

Highly-Oxygenated ON in Chamber Studies (β -pinene + NO_3)



- Highly-oxygenated ON observed in FIGAERO-CIMS with 4 – 9 oxygen atoms
- Rapid formation, likely occurs through auto-oxidation (Crouse et al., 2013; Ehn et al., 2014)

Nah et al., ES&T, 2016

ON Observed with FIGAERO-HR-ToF-CIMS

β -pinene + NO₃

Molecule-iodide adduct formula	Exact m/z
C ₁₀ H ₁₇ NO ₂ I	342.020782
C ₁₀ H ₁₂ NO ₂ I	356.000031
C ₁₀ H ₁₇ NO ₂ I	358.015686
C ₁₀ H ₁₂ NO ₂ I	360.031311
C ₁₀ H ₁₂ NO ₂ I	369.97934
C ₁₀ H ₁₂ NO ₂ I	371.994965
C ₁₀ H ₁₇ NO ₂ I	374.01062
C ₁₀ H ₁₂ NO ₂ I	376.026306
C ₁₀ H ₁₂ NO ₂ I	385.974213
C ₁₀ H ₁₂ NO ₂ I	387.989868
C ₁₀ H ₁₇ NO ₂ I	390.005524
C ₁₀ H ₁₂ NO ₂ I	392.02121
C ₁₀ H ₁₃ NO ₂ I	401.969147
C ₁₀ H ₁₂ NO ₂ I	403.984772
C ₁₀ H ₁₇ NO ₂ I	406.000427
C ₁₀ H ₁₂ NO ₂ I	408.016052
C ₁₀ H ₁₂ NO ₂ I	417.96405
C ₁₀ H ₁₂ NO ₂ I	419.979675
C ₁₀ H ₁₇ NO ₂ I	421.995361
C ₉ H ₁₂ NO ₂ I	357.979309
C ₉ H ₁₂ NO ₂ I	359.994965
C ₉ H ₁₂ NO ₂ I	373.974182
C ₉ H ₁₂ NO ₂ I	375.989868
C ₉ H ₁₇ NO ₂ I	378.005524
C ₉ H ₁₂ NO ₂ I	389.969147
C ₉ H ₁₂ NO ₂ I	391.984833
C ₉ H ₁₂ NO ₂ I	405.96405
C ₉ H ₁₂ NO ₂ I	407.979706
C ₉ H ₁₁ NO ₂ I	343.963654
C ₉ H ₁₁ NO ₂ I	345.979309
C ₉ H ₁₁ NO ₂ I	359.958588
C ₉ H ₁₂ NO ₂ I	361.974213
C ₉ H ₁₁ NO ₂ I	375.953491
C ₉ H ₁₁ NO ₂ I	377.969147
C ₉ H ₁₁ NO ₂ I	391.948395
C ₉ H ₉ NO ₂ I	313.953094
C ₉ H ₉ NO ₂ I	329.947998
C ₉ H ₁₂ NO ₂ I	331.963654
C ₉ H ₉ NO ₂ I	345.942932
C ₉ H ₁₁ NO ₂ I	347.958588
C ₉ H ₉ NO ₂ I	361.937836

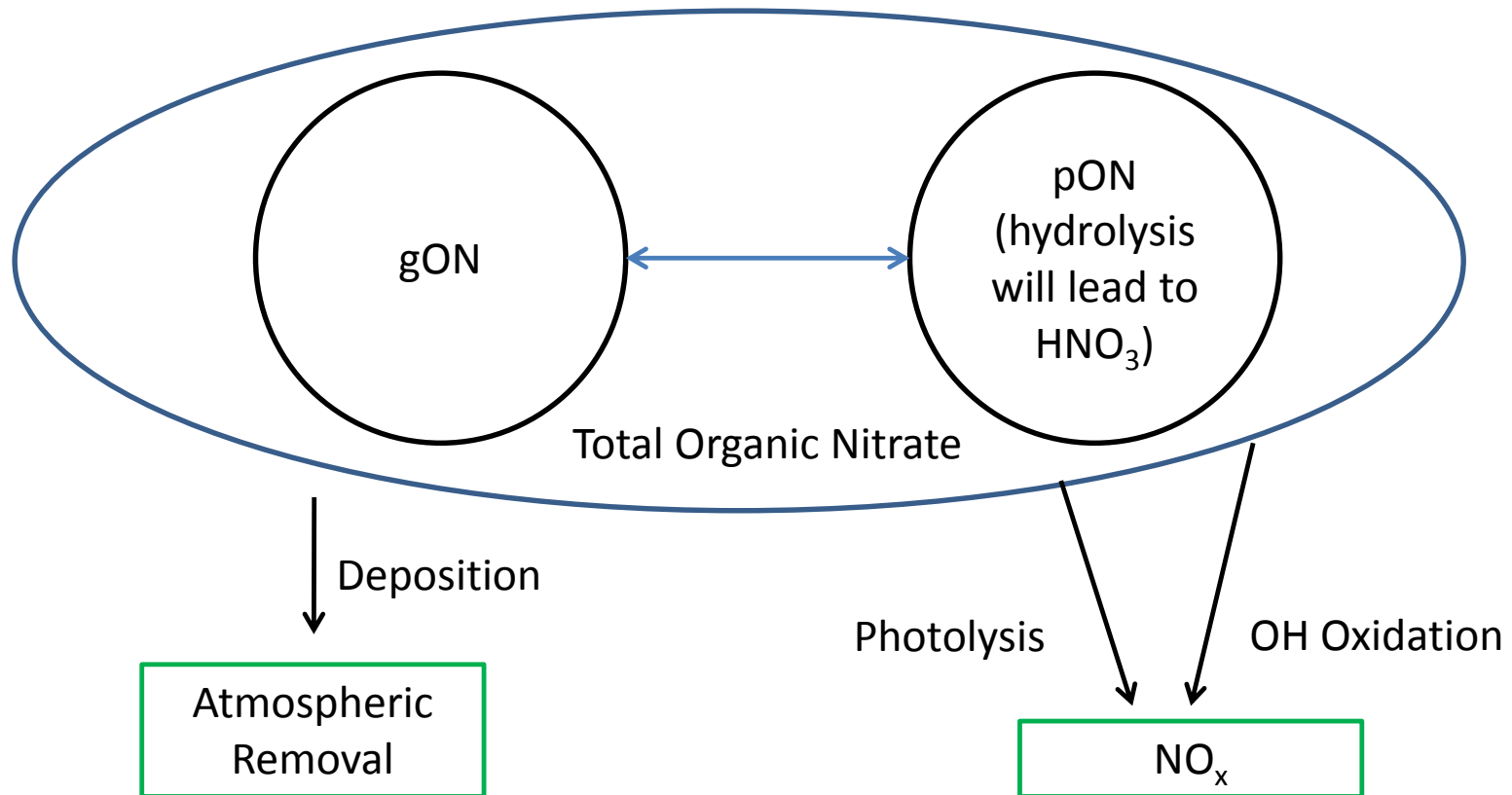
α -pinene + NO₃

Molecule-iodide adduct formula	Exact m/z
C ₁₀ H ₁₂ NO ₂ I	356.000031
C ₁₀ H ₁₂ NO ₂ I	371.994965
C ₁₀ H ₁₂ N ₂ O ₂ I	403.000763
C ₁₀ H ₁₂ NO ₂ I	419.979706
C ₉ H ₁₂ NO ₂ I	357.979309

- 41 ON observed for β -pinene+NO₃
(32 observed at SOAS, Lee et al., 2016)
- 5 ON for α -pinene+NO₃
(4 observed at SOAS, Lee et al., 2016)

NO₃ chemistry forms atmospherically relevant highly oxygenated ON

Fate of Atmospheric ON

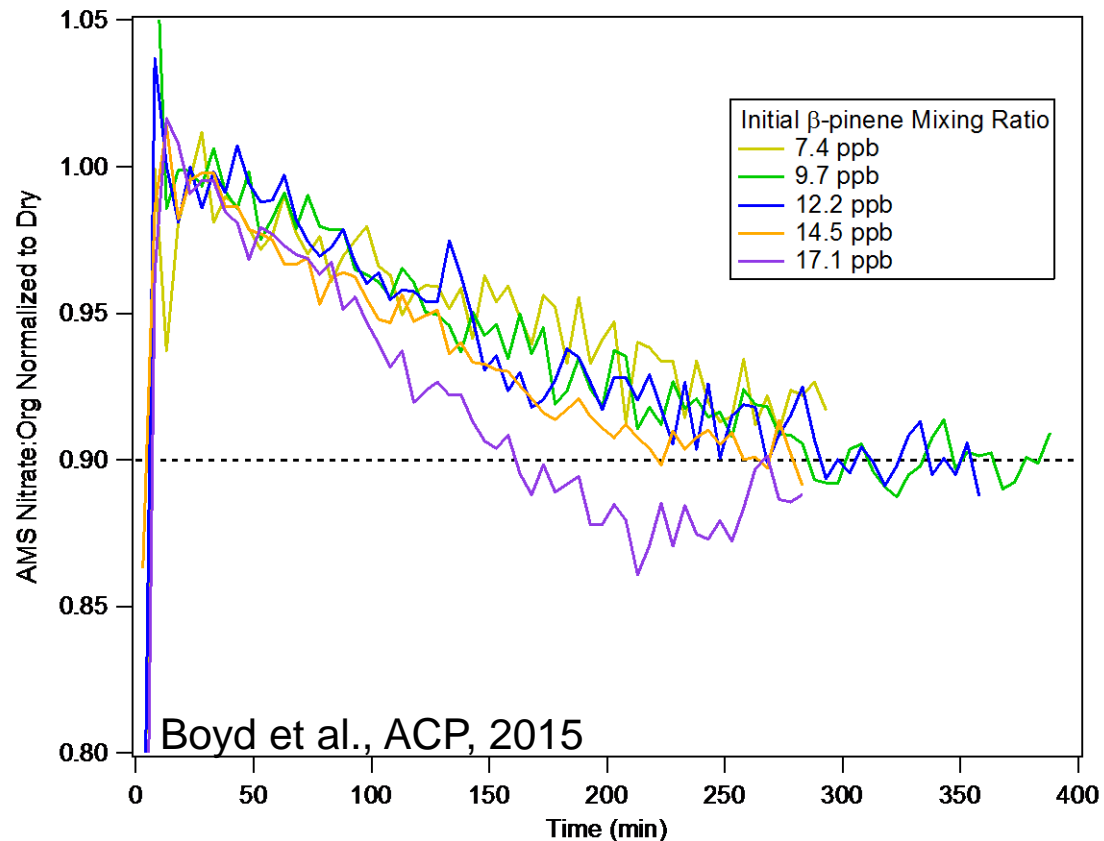


- **Aerosol ON that is not removed by deposition can either form nitric acid through hydrolysis or be released as NO_x through photolysis or OH oxidation**

1. β -pinene+NO₃: Organic Nitrate Hydrolysis

Nitrate/Org in wet expt

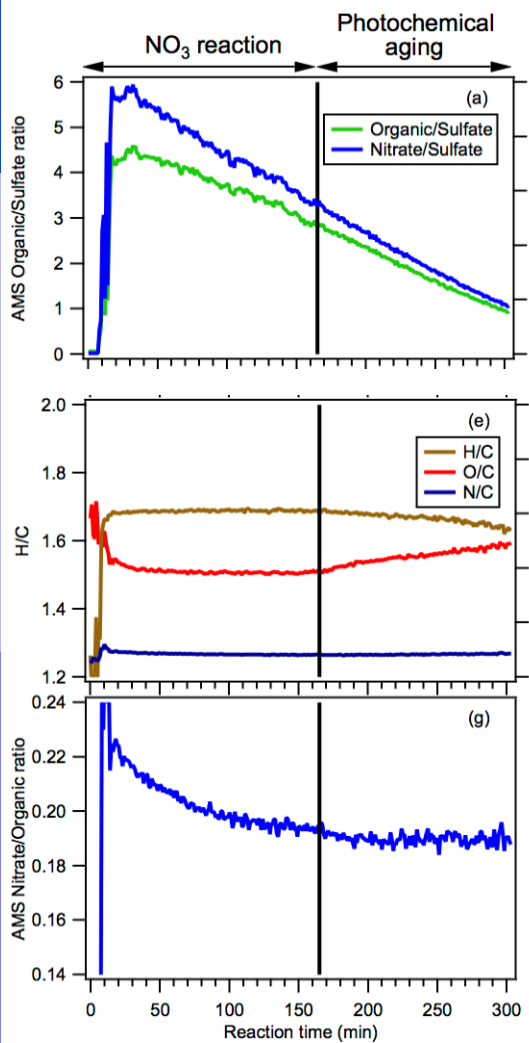
Nitrate/Org in dry expt



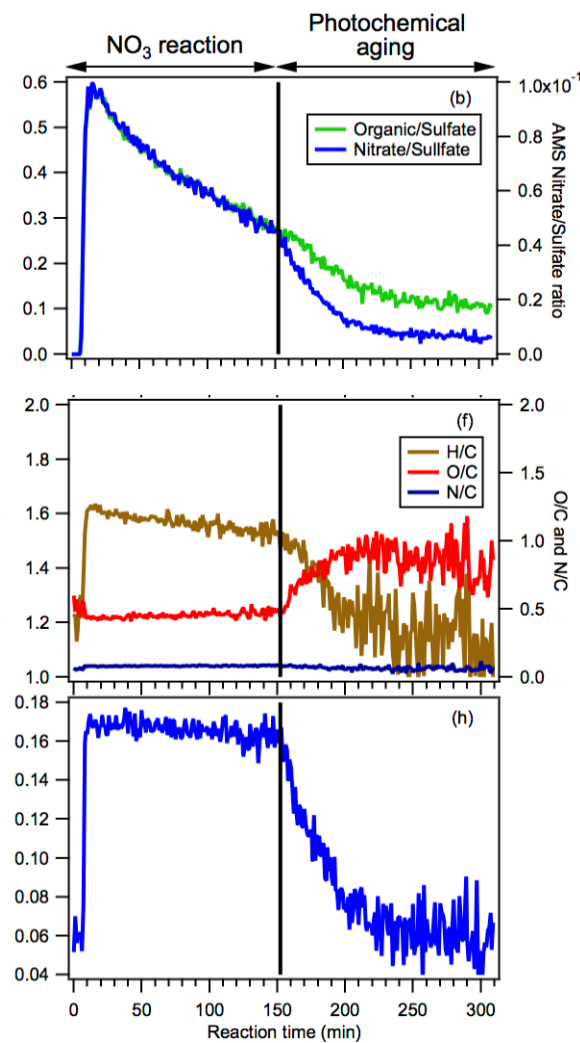
- Likely that majority (~90%) of ON is primary (which do not hydrolyze at appreciable rates)
- ~ 10% of ON hydrolyzes with a lifetime of 3-4.5 hr
 - Much higher than primary/tertiary ON ratio predicted by SOA formed from photooxidation under high NO_x conditions (Browne et al., 2013)
- **What happens to ON that do not hydrolyze? (do they get photolyzed /OH reaction?)**

2. Photochemical Aging of Nighttime Aerosol

β -pinene + NO_3



α -pinene + NO_3



- Photochemically aging, $\text{OH} + \text{h}\nu$
- β -pinene+ NO_3 SOA: photochemical aging has little effect
- α -pinene+ NO_3 : a large fraction of reactive nitrogen is released from the α -pinene SOA back to the gas phase during photooxidation.

Conclusions

- LO-OOA (19-34%) : likely originates from monoterpenes, and its formation could be controlled by nighttime NO_3 chemistry (NO_x effect)
- ON contributes up to 12% of ambient OA in SE US in summer
- β -pinene+ NO_3 reaction
 - FIGAERO-HR-ToF-CIMS: Formation of highly oxygenated ON species in both gas- and particle-phase, many of which observed at SOAS
 - This reaction likely contributes substantially to ambient LO-OOA and ON
 - Peroxy radical fate and RH does not have a strong effect on SOA yield
- Hydrolysis: ~90% of the ON formed from the β -pinene+ NO_3 reaction are primary nitrates, do not hydrolyze at appreciable rates
- Atmospheric perturbations
 - Particulate ON from β -pinene+ NO_3 : NO_x sinks
 - Particulate ON from α -pinene+ NO_3 : photochemical oxidation may be an important atmospheric NO_x source in the day

Laboratory studies should be an integrated part of field studies

Acknowledgement

Georgia Tech

Hongyu Guo, Aikaterini Bougiatioti, Kate Cerully,
James Hite, Rodney Weber, Athanasios Nenes

Emory University

Mitchel Klein

UC Berkeley

Gabriel Isaacman-VanWertz, Kevin Olson,
Allen Goldstein

Aerosol Dynamics

Nathan M. Kreisberg, Susanne V. Hering

NCAR

Christoph Knote

NOAA and CIRES

Abigail Koss, Joost de Gouw

ARA

Karsten Baumann

Kent State University

Shan-Hu Lee

University of Kentucky

Alexis Eugene
Marcelo Guzman

Chris Boyd Theodora Nah Lu Xu

