Detection of Organic Nitrates in Ambient PM

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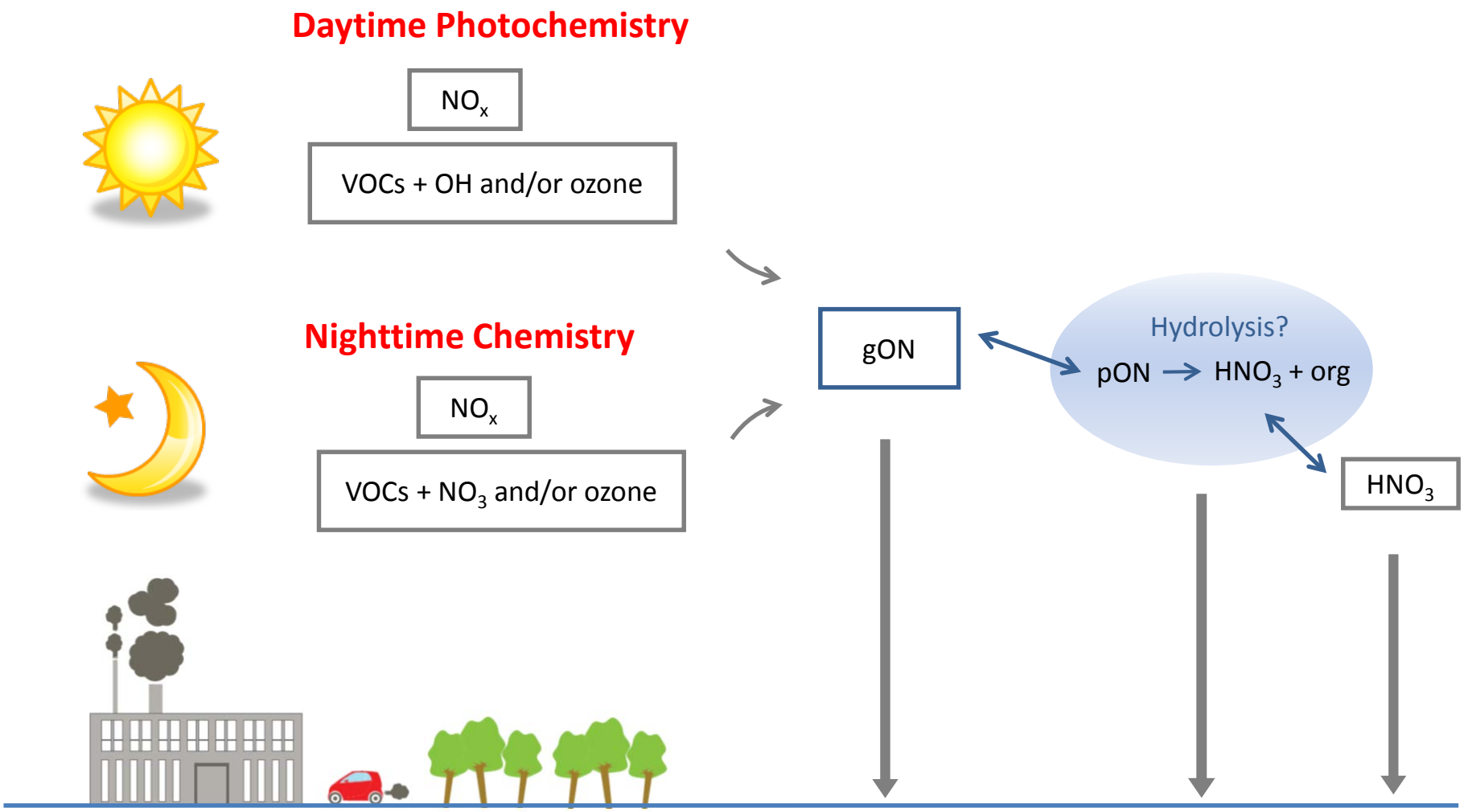
AMS Users Meeting, 2017

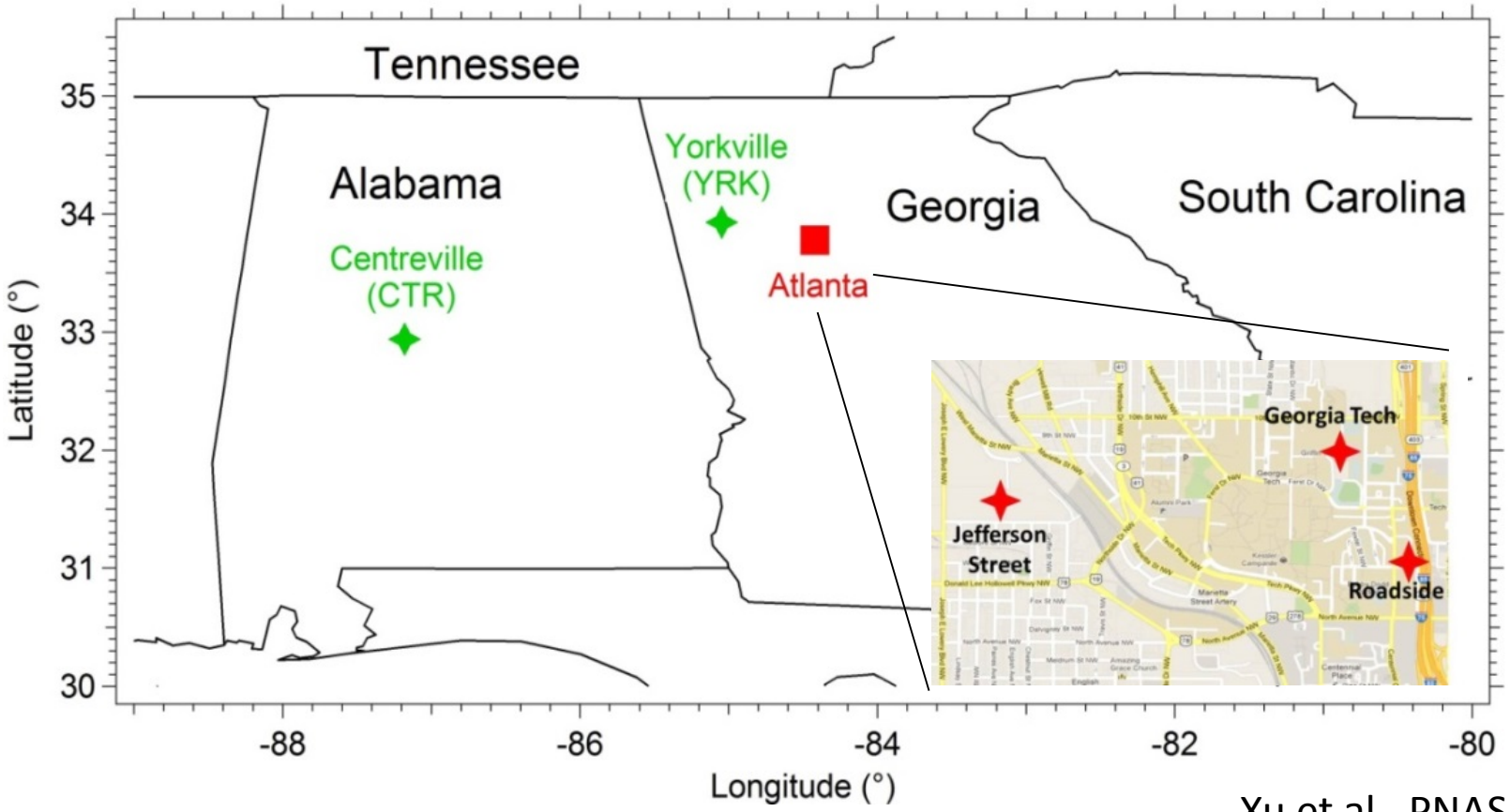
Georgia Tech

Role of NO_x: Organic Nitrates



Field Measurements: SOAS and SCAPE

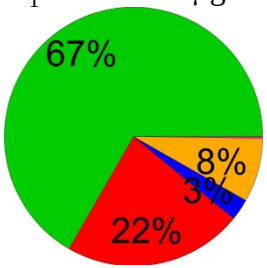
- Southern Oxidant and Aerosol Study (SOAS)
  - 2013 June - July
  - Centreville (rural Alabama)
- Southeastern Center of Air Pollution and Epidemiology study (SCAPE)
  - 2012 May - 2013 Feb
  - Greater Atlanta Area (urban and rural)



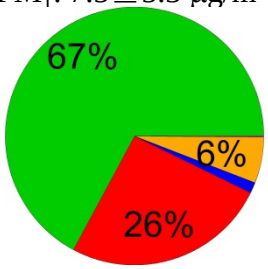
Xu et al., PNAS, 2015
Xu et al, ACP, 2015

Composition of Ambient Non-refractory PM_1 in SE US

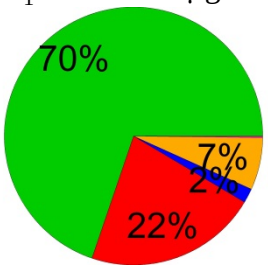
Jefferson Street (May)
PM_1: 13.6±5.6 μg/m³



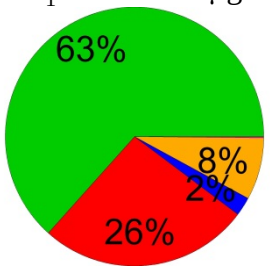
Centreville (June)
PM_1: 7.5±5.3 μg/m³

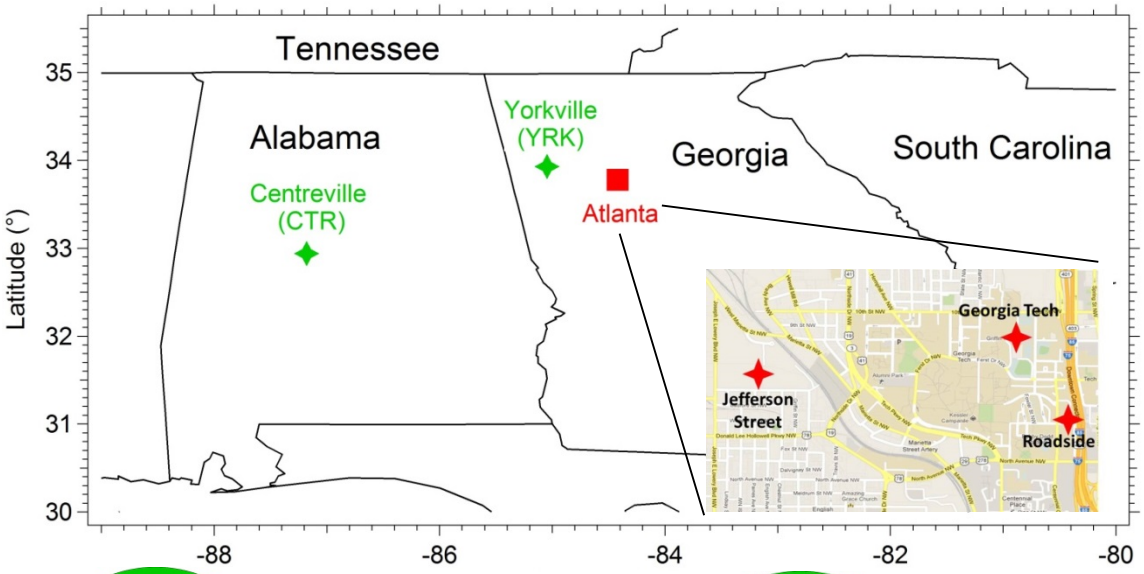


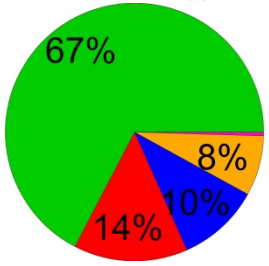
Yorkville (July)
PM_1: 16.0±8.3 μg/m³



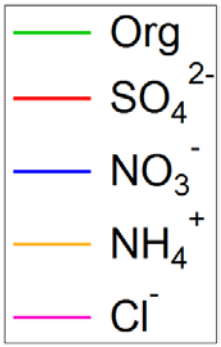
Georgia Tech (Aug)
PM_1: 15.2±6.7 μg/m³

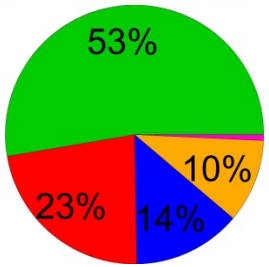




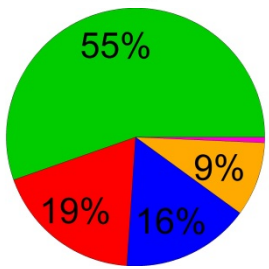


Jefferson Street (Nov)
PM_1: 11.8±6.1 μg/m³





Yorkville (Dec)
PM_1: 6.0±3.8 μg/m³

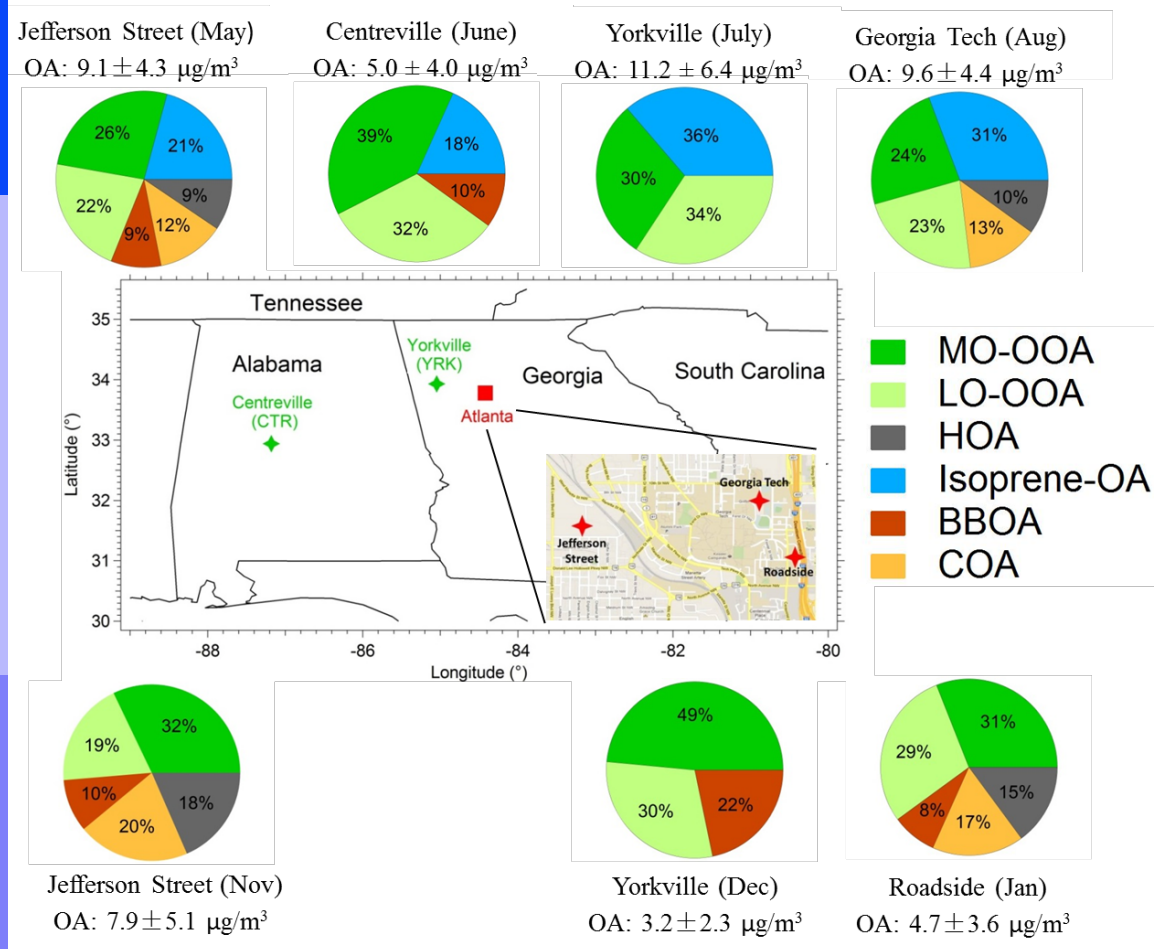


Roadside (Jan)
PM_1: 8.5±5.5 μg/m³

- OA is the dominant component in PM_1 (>50%).
- PM_1 composition varies spatially and seasonally

Xu et al., PNAS, 2015

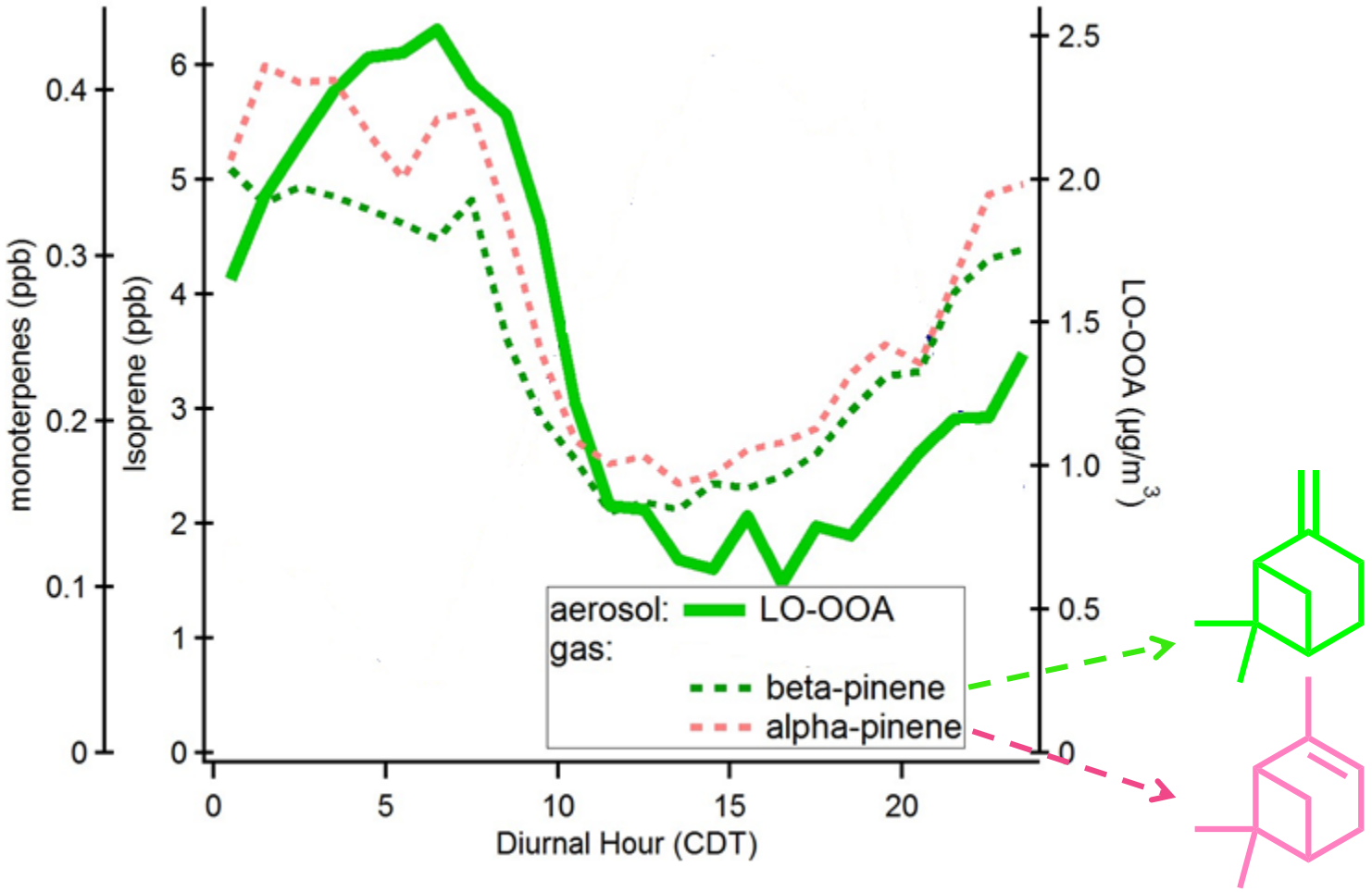
PMF Analysis: OA Source Apportionment in the SE US



- 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



1) LO-OOA has similar diurnal trend as monoterpenes (α-pinene and β-pinene)
2) NO_3 radical (a product of NO_2 and O_3) is the major oxidation at night.
3) Hypothesis: Nighttime increase is caused by α-pinene/β-pinene + NO_3 radical

Estimation of $NO3_{org}$ (i.e., $-ONO_2$ concentration that arises from organic nitrates)

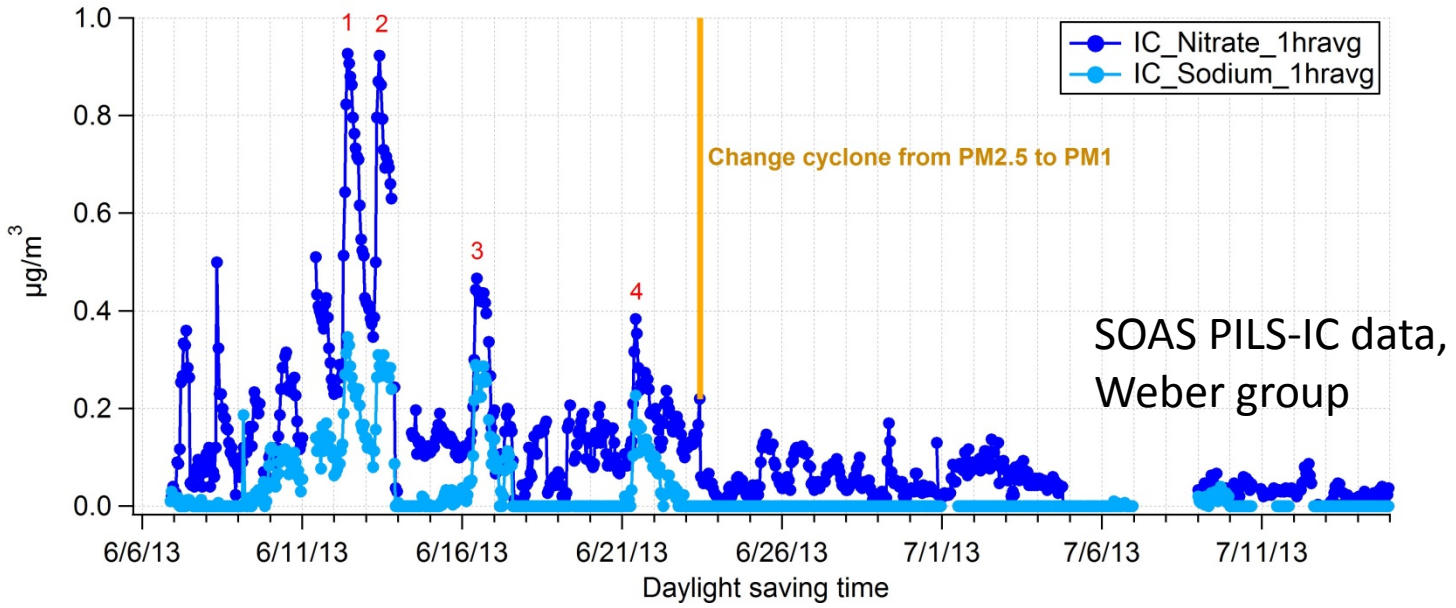
Three independent methods

1. **AMS-IC method**: AMS total nitrate - PILS inorganic nitrate
2. **NO^+/NO_2^+ ratio method** (NO_x^+ method) (Farmer et al., 2010)
3. **PMF method**: include NO^+ and NO_2^+ in PMF analysis

Xu et al., ACP, 2015

Method 1: AMS-IC method

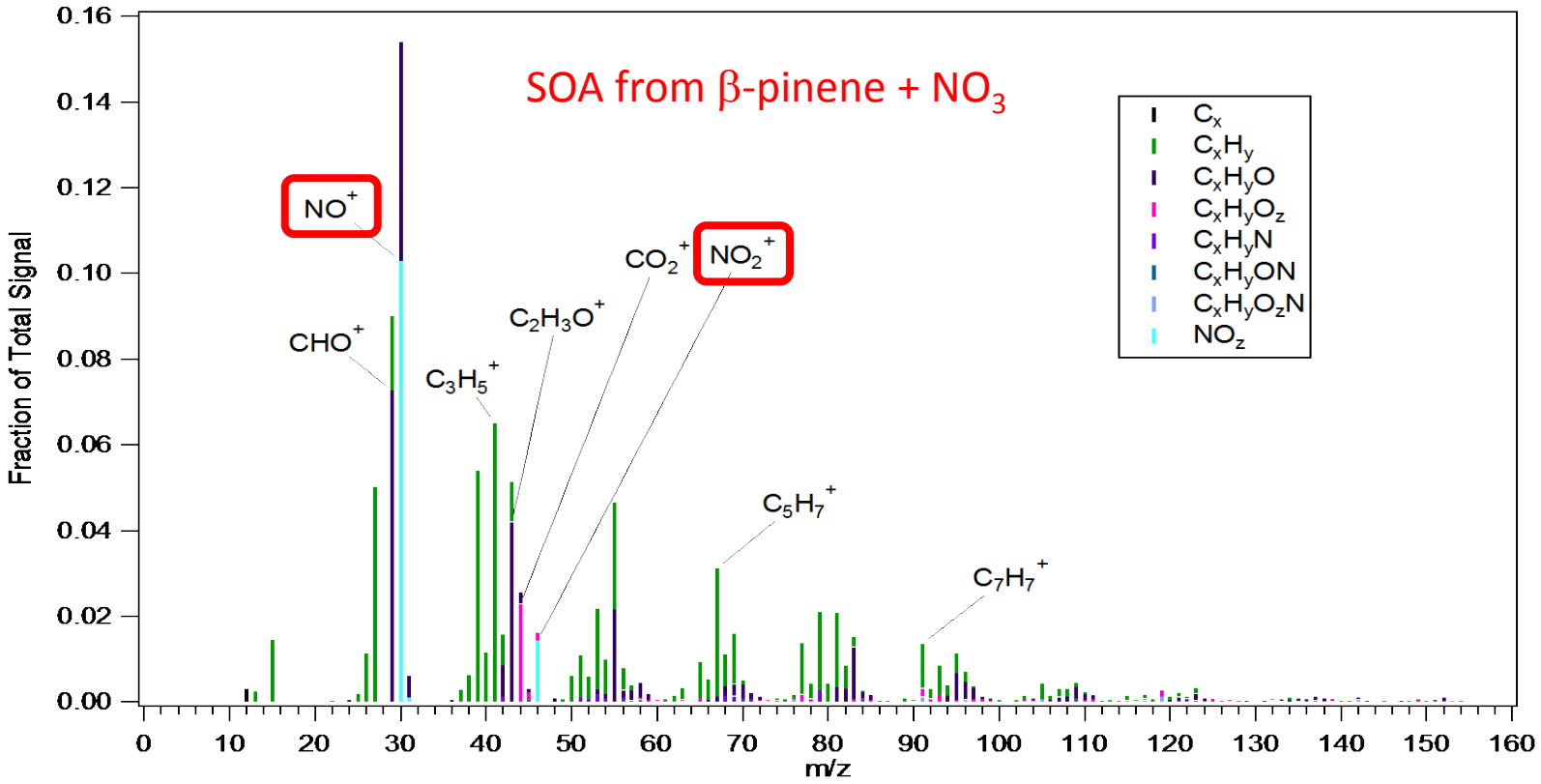
- AMS total nitrate – PILC inorganic nitrate
- PM1 cyclone used for PILS-IC (to match with AMS cut-size)
- Caution: interference from particles > 1um (e.g., $NaNO_3$ in mineral dust)



- Sodium measured by PILS with PM1 cyclone is negligible and is below detection limit (0.07 ug/m^3)
- Can use the AMS-IC method for SOAS data

Xu et al., ACP, 2015

Method 2: NO^+/NO_2^+ ratio method (NO_x^+ method)



- Large fraction of nitrate species at NO^+ (*m/z* 30) and NO_2^+ (*m/z* 46)
- NO^+ / NO_2^+ ratio = 4.8 – 10.2 (biogenic organic nitrates)

Boyd et al., ACP, 2015

Method 2: NO^+/NO_2^+ ratio method (NO_x^+ method)

Eqt from Farmer et al. (2010)

NO^+/NO_2^+ of ambient OA

$$NO_{2,org} = \frac{NO_{2,meas} \times (R_{meas} - R_{AN})}{R_{ON} - R_{AN}}$$

$$NO_{org} = R_{ON} \times NO_{2,org}$$

NO^+/NO_2^+ for ammonium nitrate (~ 2)

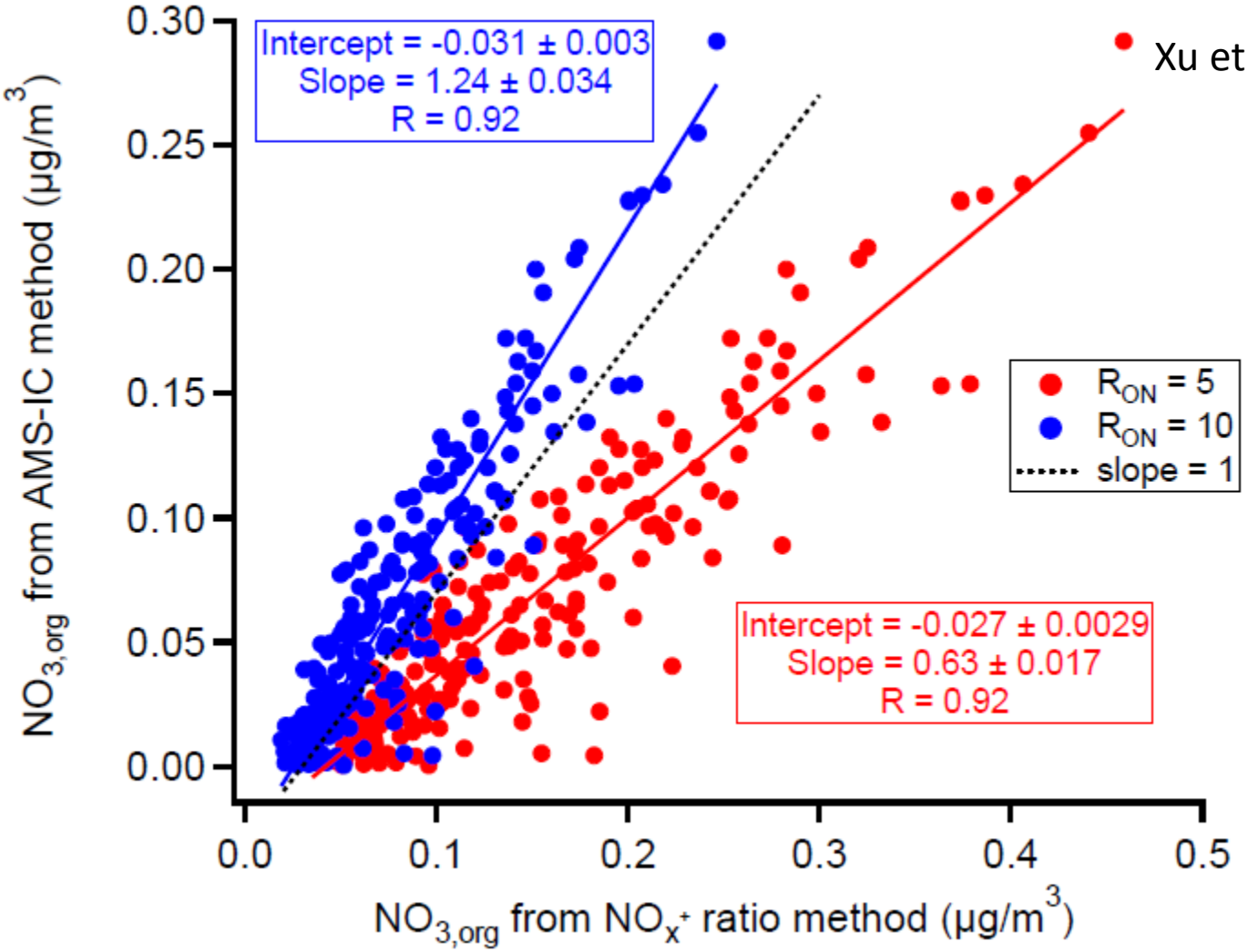
NO^+/NO_2^+ for organic nitrate (depends on VOC, instrument, etc)

R_{ON} and R_{AN} values appears to have some instrument dependence, but their ratio (R_{ON} / R_{AN}) might be more instrument independent (Fry et al., 2013)

1. Determine R_{AN} from IE calibrations (e.g., our RAN ranges from 1.93 to 2.73, average 2.28)
2. Use R_{ON}/R_{AN} values reported for isoprene organic nitrates (2.08) and b-pinene organic nitrates (3.70-4.17) (Boyd et al., 2015, Bruns et al., 2010; Fry et al., 2009)
3. Multiple average R_{ON} values (from IE cal) with these R_{ON}/R_{AN} values
4. **Obtain R_{ON} =5 and R_{ON} =10 as lower and upper bounds**

Xu et al., ACP, 2015

Compare AMS-IC method and NO_x^+ method



Xu et al., ACP, 2015

Method 3: $PMF_{org+NO3}$ method

Perform PMF analysis on organic mass spectra together with NO^+ and $NO2^+$ ions

$$[NO^+_{org}] = \sum([\text{OA factor}]_i \times f\_NO_i)$$

$$[NO^+_{2,org}] = \sum([\text{OA factor}]_i \times f\_NO_{2,i})$$

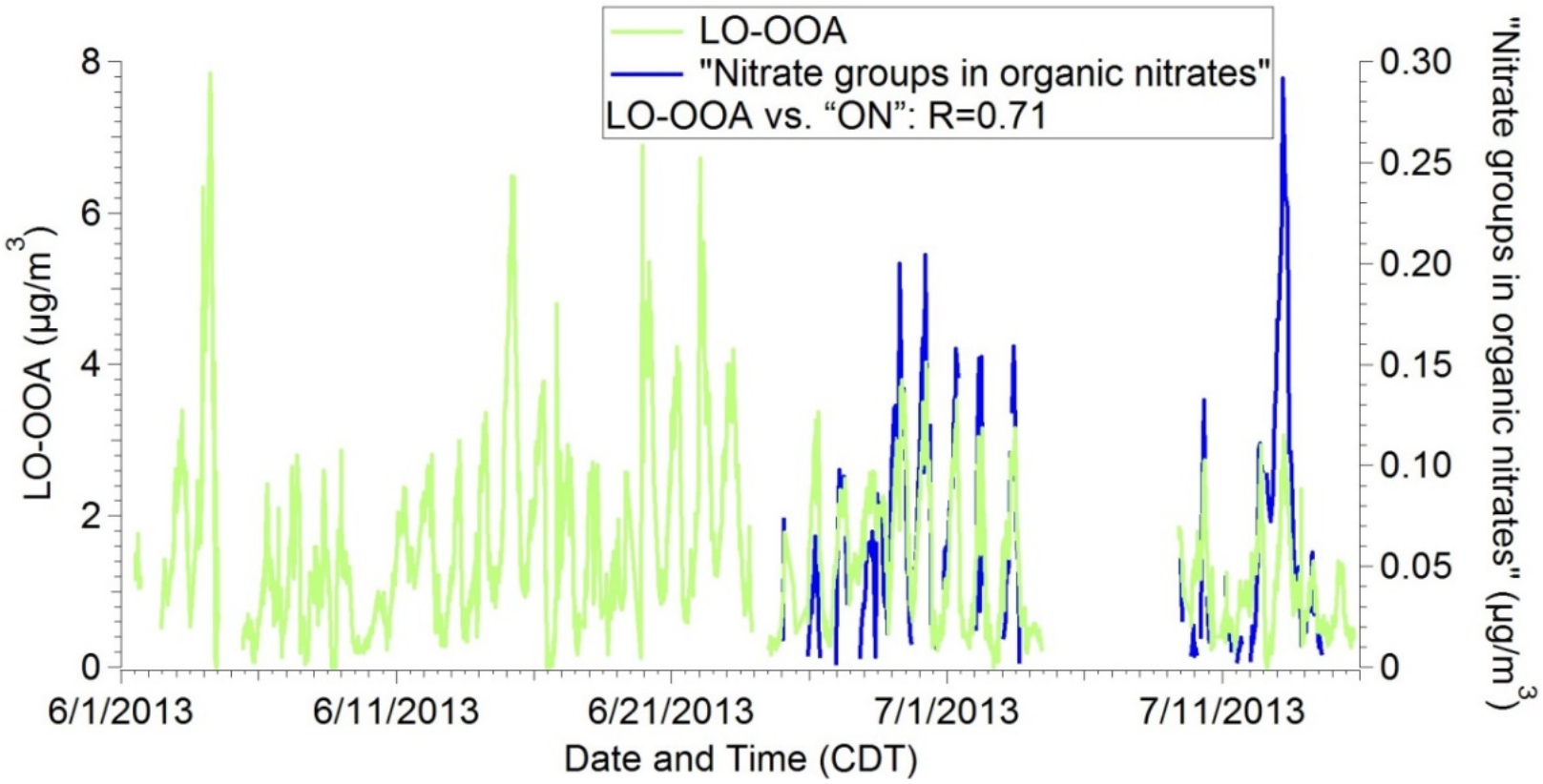
$[\text{OA factor}]_i$ is the mass concentration of *i*th OA factor
f_NO_i and $f\_NO_{2,i}$ are the mass fraction of NO^+ and NO_2^+, respectively, in *i*th OA factor.

Often resolve a nitrate inorganic factor NIA (previously observed in Sun e al., 2012, Hao et al., 2014)

Xu et al., ACP, 2015

LO-OOA and organic nitrates

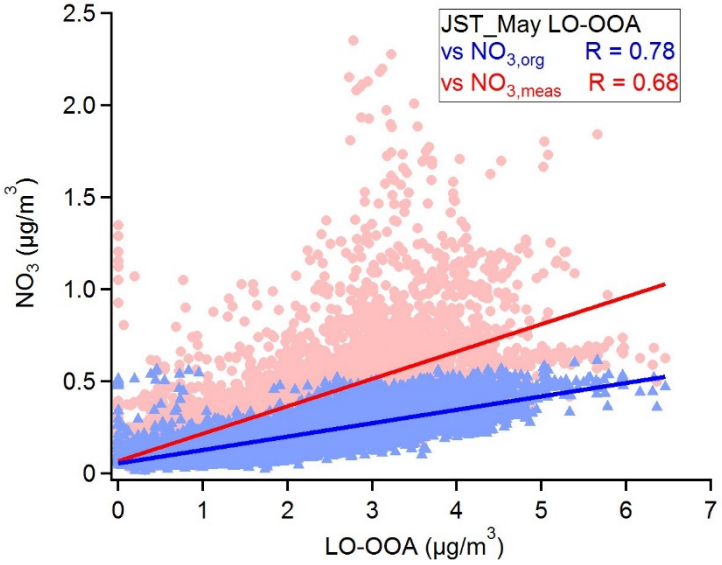
Xu et al., PNAS, 2015

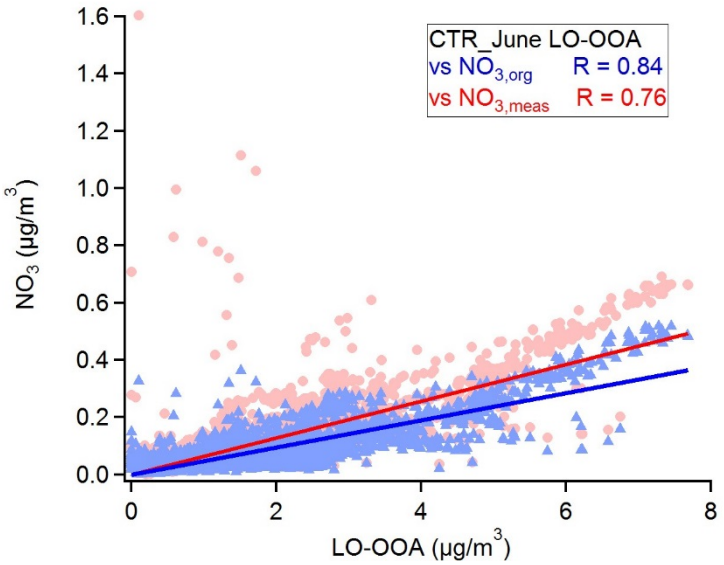


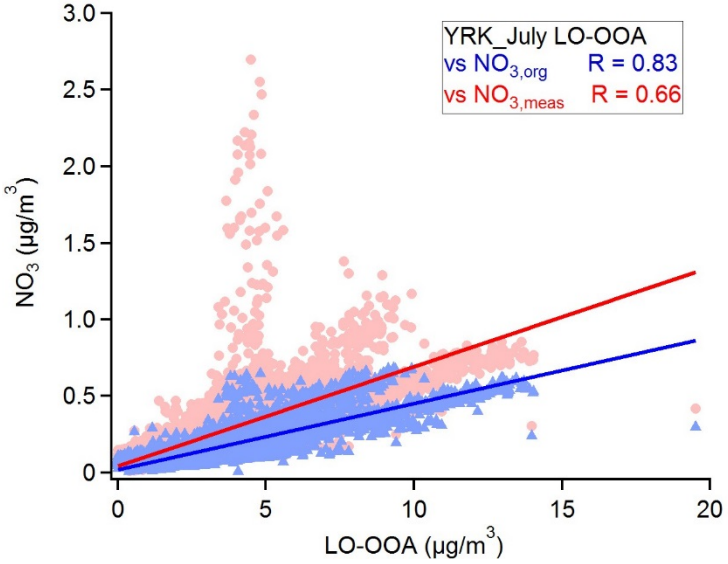
- LO-OOA is strongly correlated with organic nitrates
- **Contribution of monoterpenes + $NO_3^\bullet$ chemistry to LO-OOA**

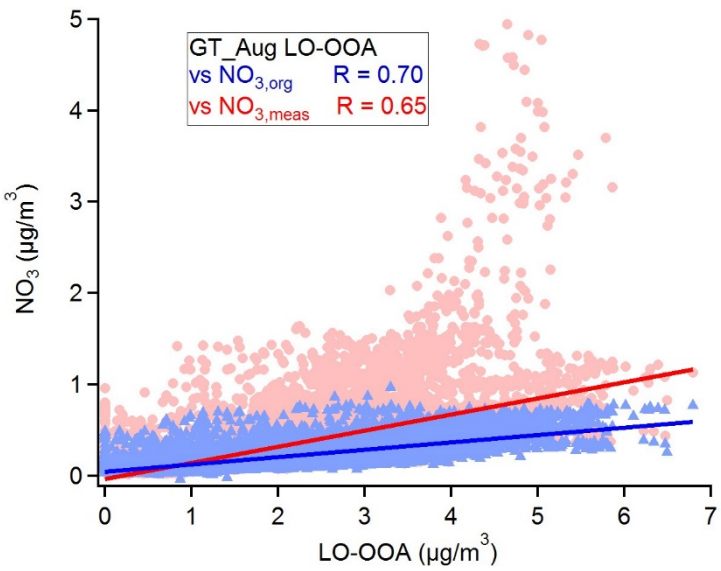
Correlation with LO-OOA

Xu et al., ACP, 2015



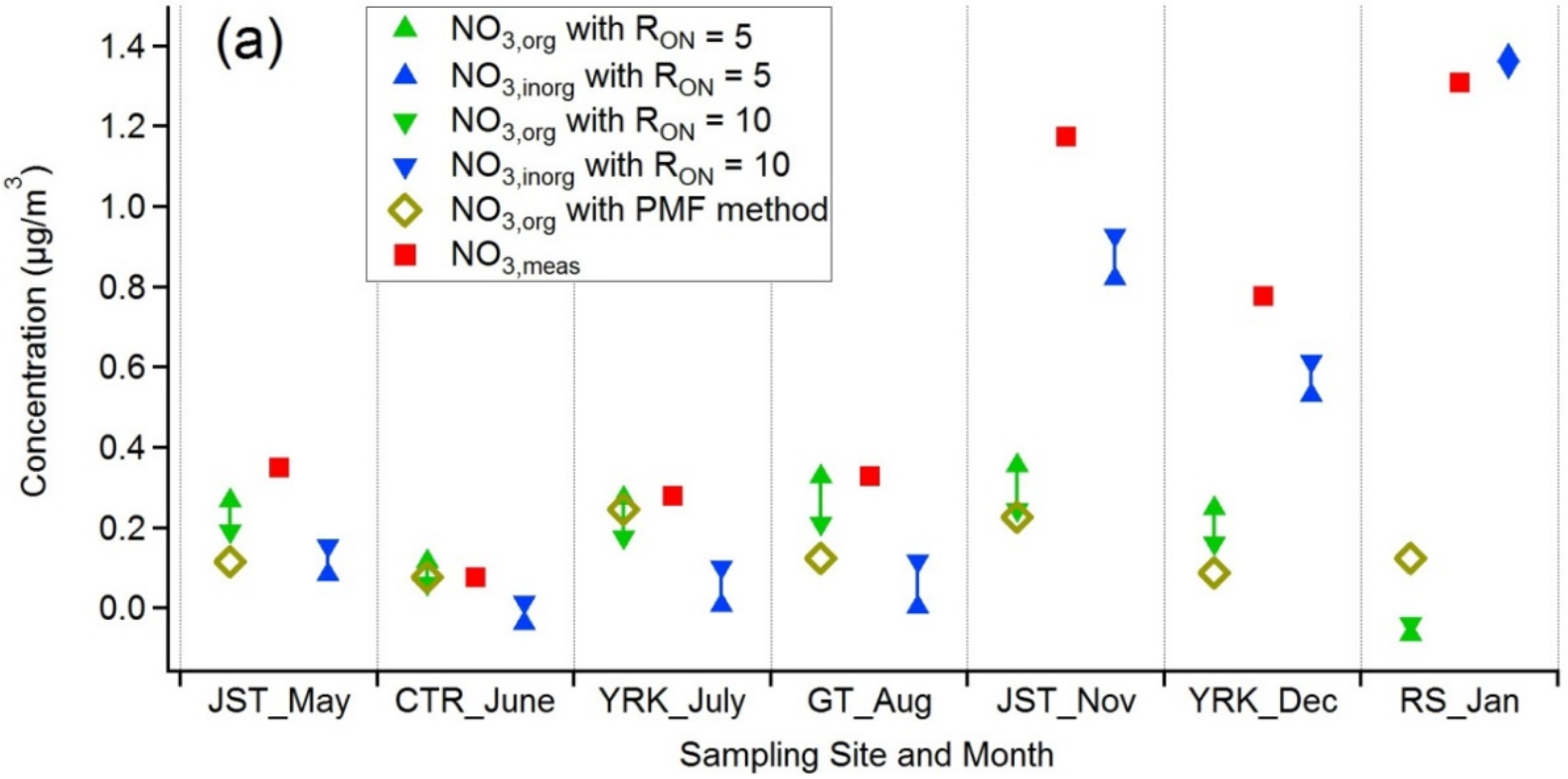






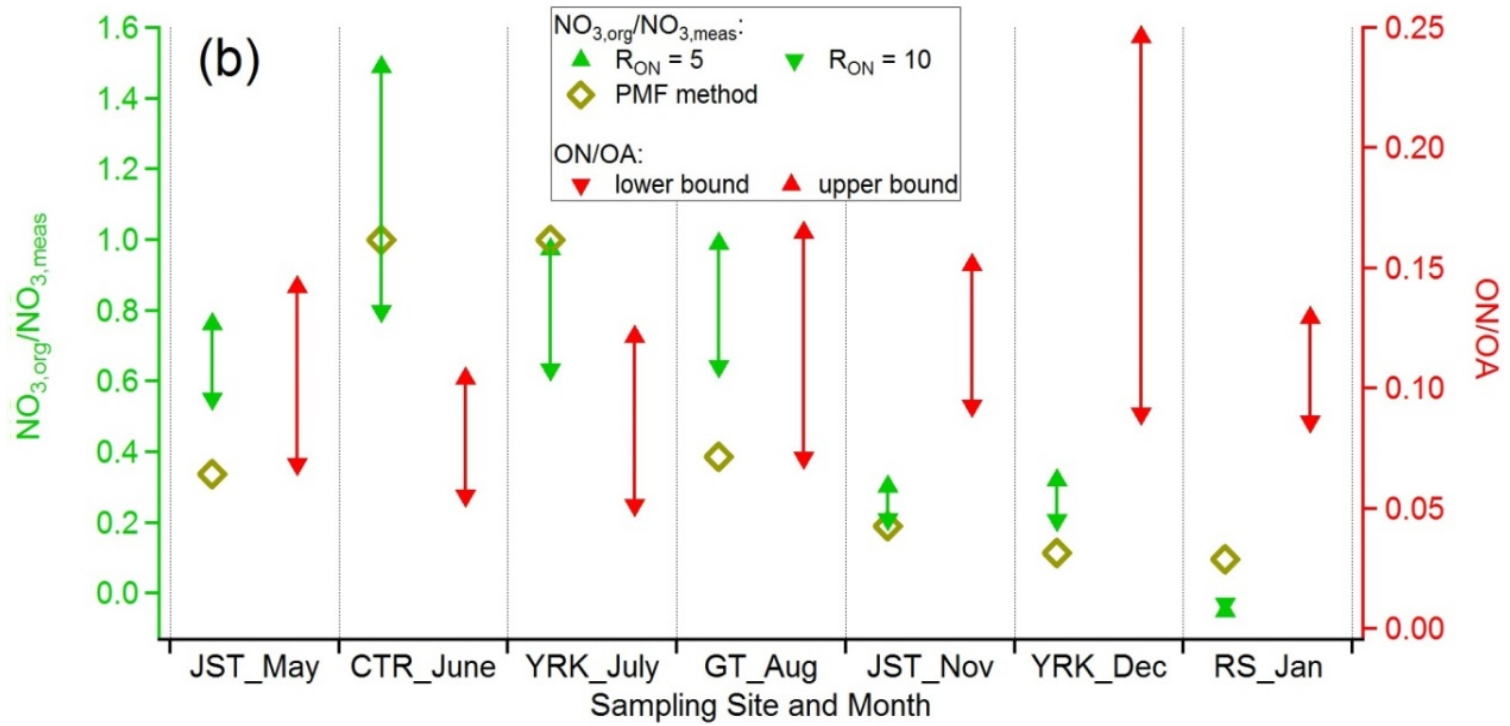
$NO3_{org}$ and $NO3_{inorg}$ in the Southeast US

- Concentration of "nitrate groups" (-ONO2)
- **Organic origin:** similar amount year round, is ~ 0.2 ug/m^3
- **Inorganic origin:** higher in winter months, ~ 0.8 – 1.4 ug/m^3



Xu et al., ACP, 2015

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

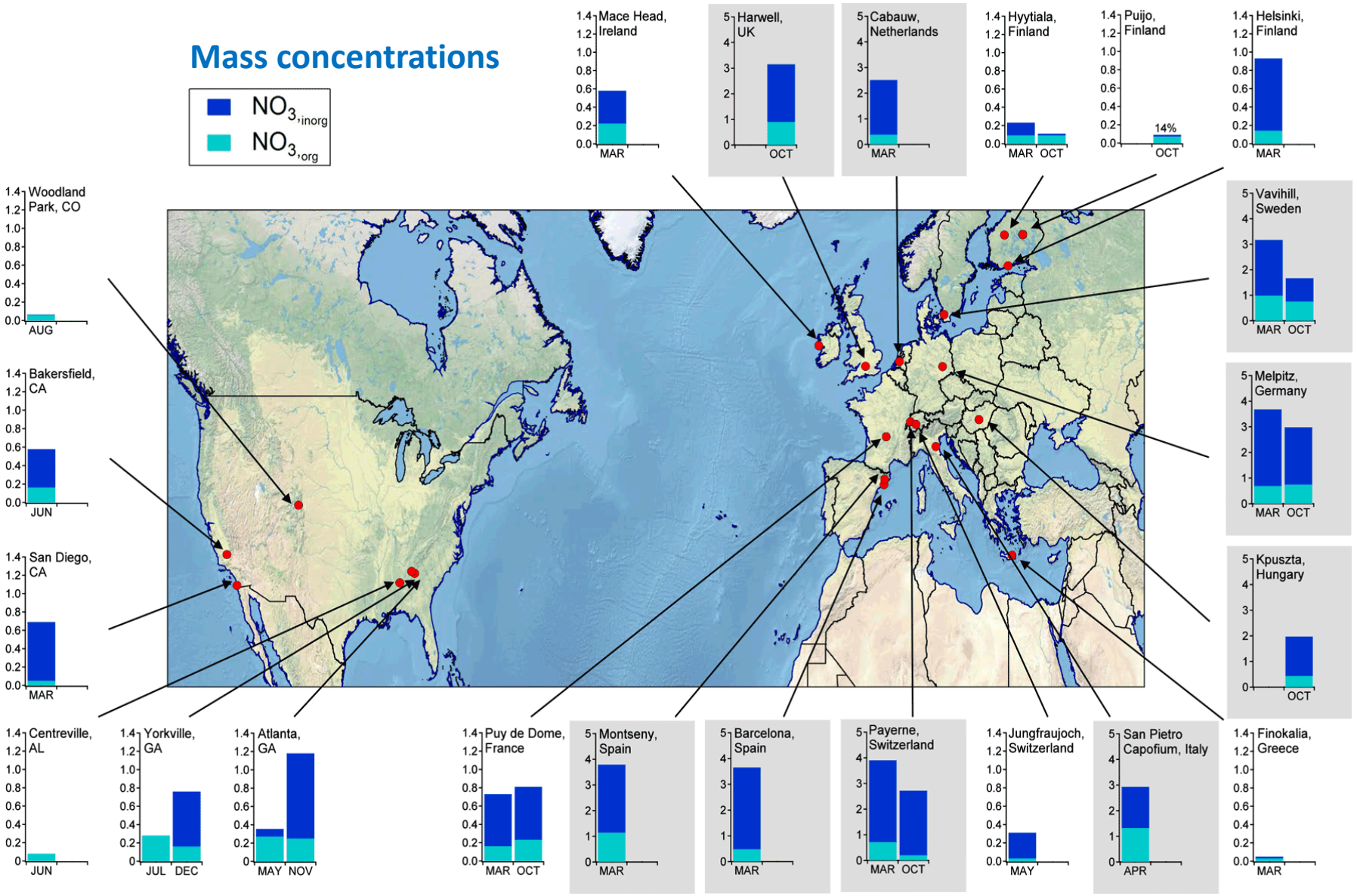
Atmos. Chem. Phys., 17, 2103–2162, 2017
www.atmos-chem-phys.net/17/2103/2017/
doi:10.5194/acp-17-2103-2017

Atmospheric Chemistry and Physics Open Access EGU

Nitrate radicals and biogenic volatile organic compounds: oxidation, mechanisms, and organic aerosol

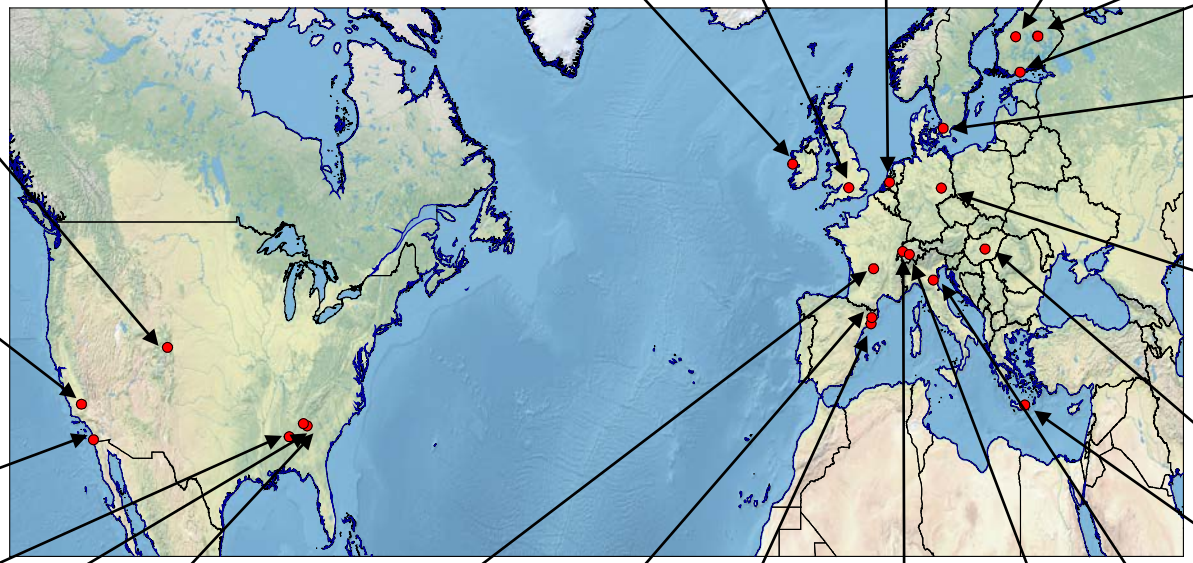
Nga Lee Ng[1,2], Steven S. Brown[3,4], Alexander T. Archibald[5], Elliot Atlas[6], Ronald C. Cohen[7], John N. Crowley[8], Douglas A. Day[9,4], Neil M. Donahue[10], Juliane L. Fry[11], Hendrik Fuchs[12], Robert J. Griffin[13], Marcelo I. Guzman[14], Hartmut Herrmann[15], Alma Hodzic[16], Yoshiteru Iinuma[15], José L. Jimenez[9,4], Astrid Kiendler-Scharr[12], Ben H. Lee[17], Deborah J. Luecken[18], Jingqiu Mao[19,20,a], Robert McLaren[21], Anke Mutzel[15], Hans D. Osthoff[22], Bin Ouyang[23], Benedicte Picquet-Varrault[24], Ulrich Platt[25], Havala O. T. Pye[18], Yinon Rudich[26], Rebecca H. Schwantes[27], Manabu Shiraiwa[28], Jochen Stutz[29], Joel A. Thornton[17], Andreas Tilgner[15], Brent J. Williams[30], and Rahul A. Zaveri[31]

Ng et al., ACP, 2017



Ng et al., ACP, 2017

Percentage of organic nitrates (by mass) in ambient OA



Hyytiala, Finland (Mar): 15% / 85%

Mace Head, Ireland (May): 47% / 53%

Harwell, UK (Oct): 63% / 37%

Cabauw, Netherlands (Mar): 67% / 33%

(Oct): 23% / 77%

Puijo, Finland (Oct): 14% / 86%

Helsinki, Finland (Mar): 11% / 89%

Woodland Park, CO (Aug): 9% / 91%

Vavihill, Sweden (Mar): 58% / 42%

(Oct): 67% / 33%

Bakersfield, CA (Jun): 23% / 77%

Melpitz, Germany (Mar): 73% / 27%

(Oct): 43% / 57%

San Diego, CA (Mar): 11% / 89%

Kpuszta, Hungary (Oct): 18% / 82%

Centreville, AL (Jun): 10% / 90%

Yorkville, GA (Jul): 12% / 88%

Atlanta, GA (May): 14% / 86%

Puy de Dome, France (Mar): 63% / 37%

Montseny, Spain (Mar): 67% / 33%

Barcelona, Spain (Mar): 13% / 87%

Payerne, Switzerland (Mar): 39% / 61%

Jungfraujoch, Switzerland (May): 8% / 92%

San Pietro Capofium, Italy (Apr): 77% / 23%

Finokalia, Greece (Mar): 5% / 95%

(Dec): 25% / 75%

(Nov): 15% / 85%

(Oct): 29% / 71%

(Oct): 8% / 92%

Back to the lab

Fundamental laboratory studies are important

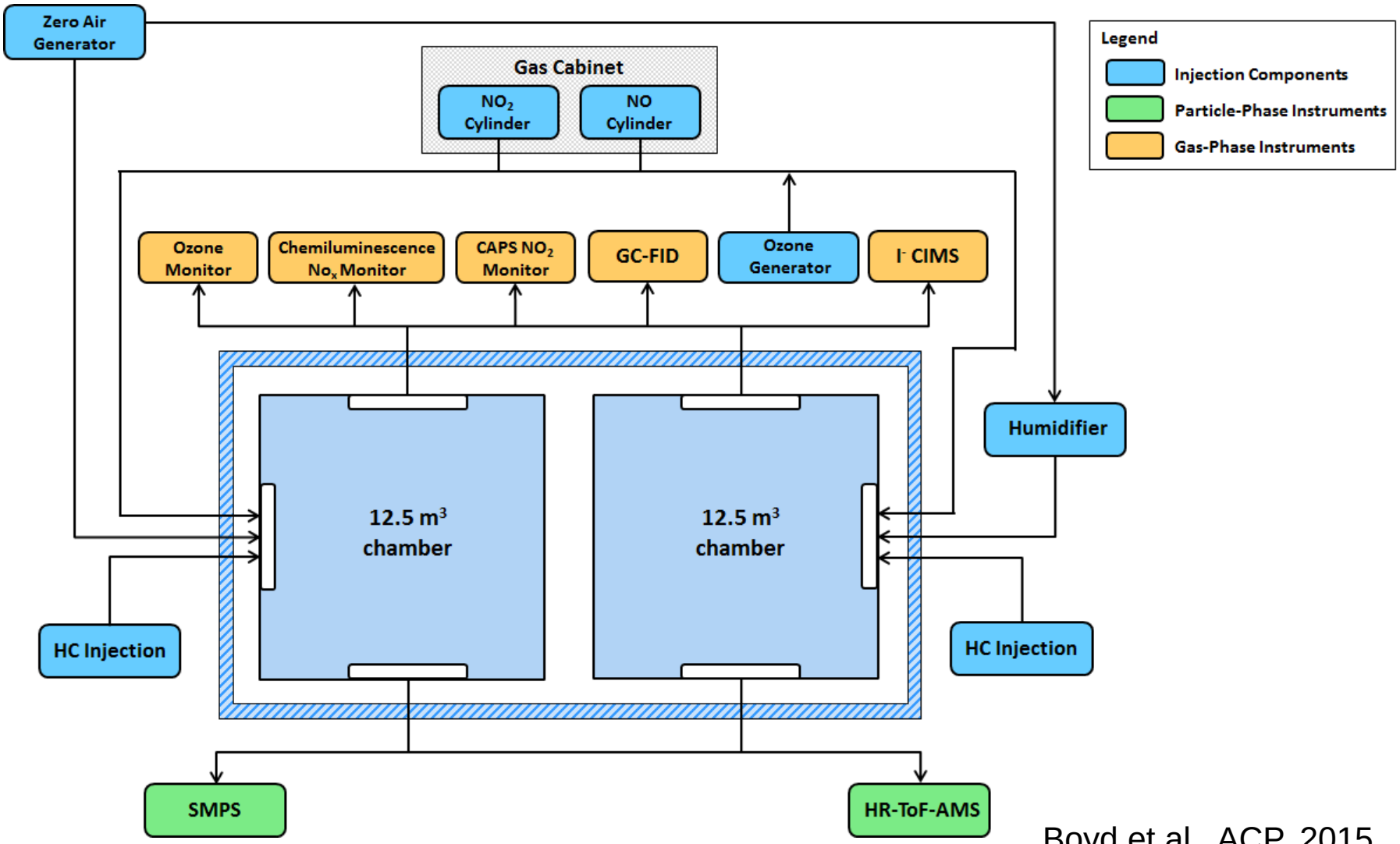
- Monoterpenes + nitrate radical oxidation (SOA yields, formation mechanisms, organic nitrates, formation/fates)

High concentration of β-pinene in SOAS, need laboratory studies of β-pinene+NO_3 under conditions relevant to SE US.

- High RH
- Highly acidic particles
- "Low-NOx" chemistry (RO_2+HO_2)
- Loadings ~ 10 μg/m^3

Georgia Tech Environmental Chamber Facility

Dual chamber facility, UV + sunlight lamps, temperature range 4- 40 ^{o}C.



Boyd et al., ACP, 2015

Georgia Tech Environmental Chamber Facility

http://www.coe.gatech.edu/news/air-we-breathe

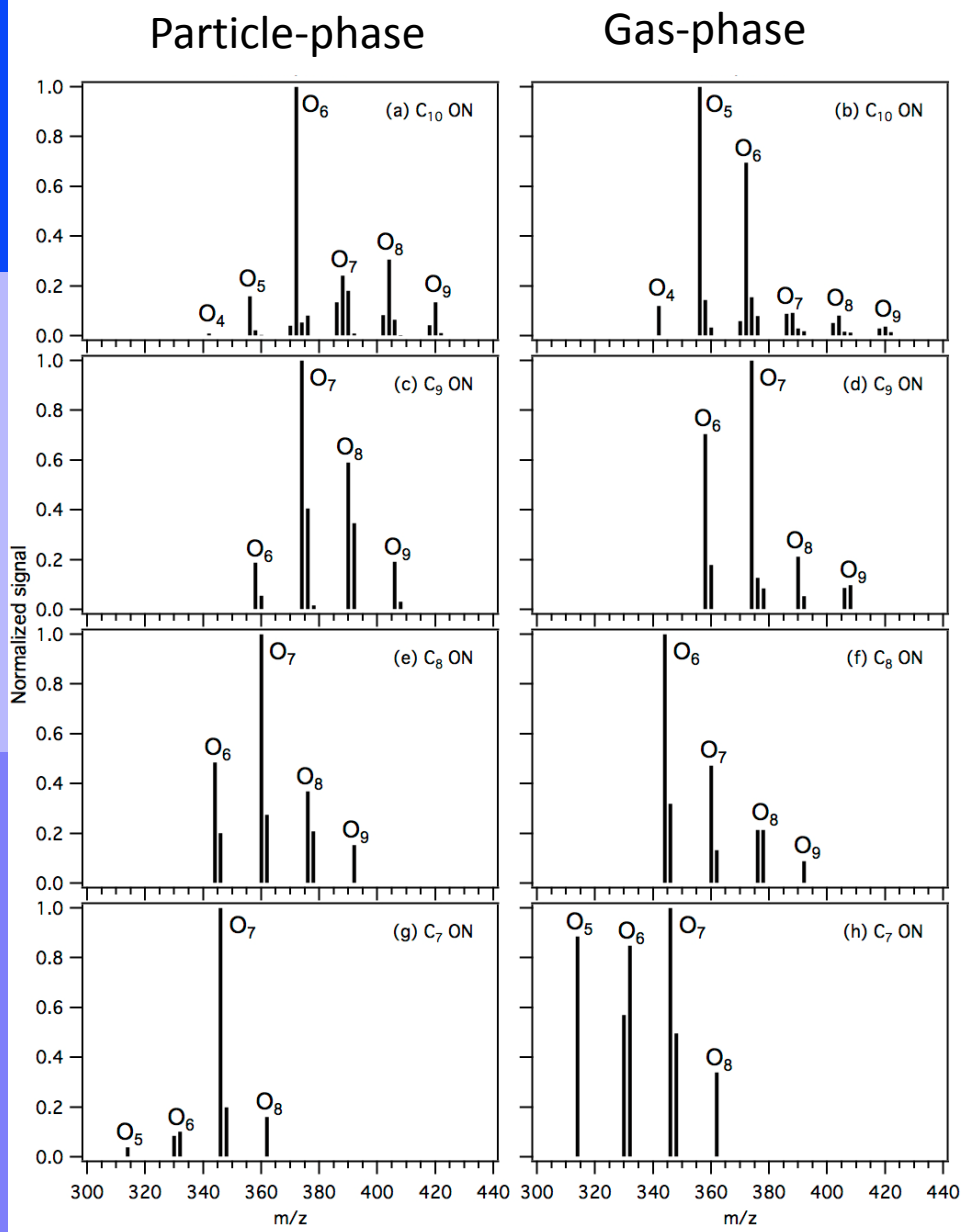
Gas-phase measurements

- HR-ToF-CIMS
- (Q-CIMS)
- GC-FID
- O_3 monitor
- Chemilumnescence $NO/NO_2/NO_x$ analyzer
- CAPS NO_2 monitor

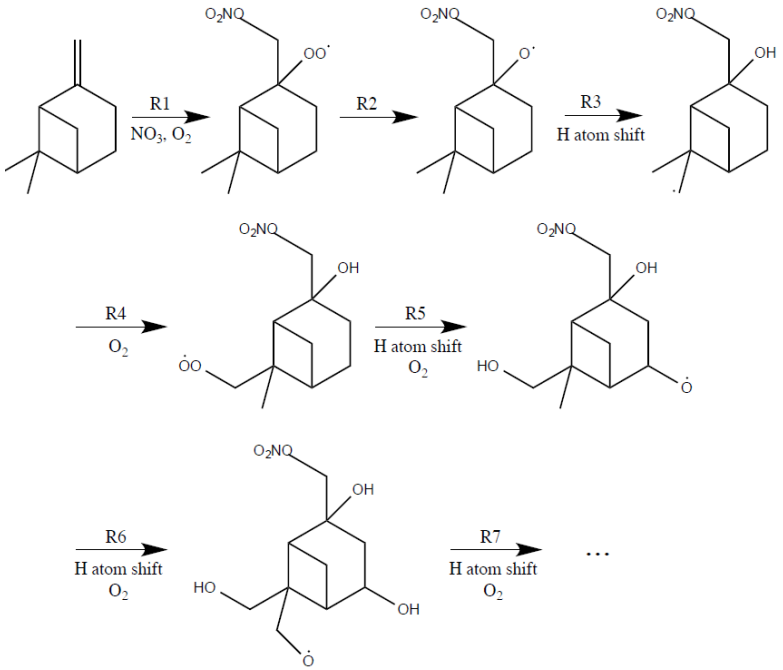
Particle-phase measurements

- HR-ToF-AMS
- FIGAERO-HR-ToF-CIMS
- (ACSM)
- SMPS
- CPC
- Offline filter characterization

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

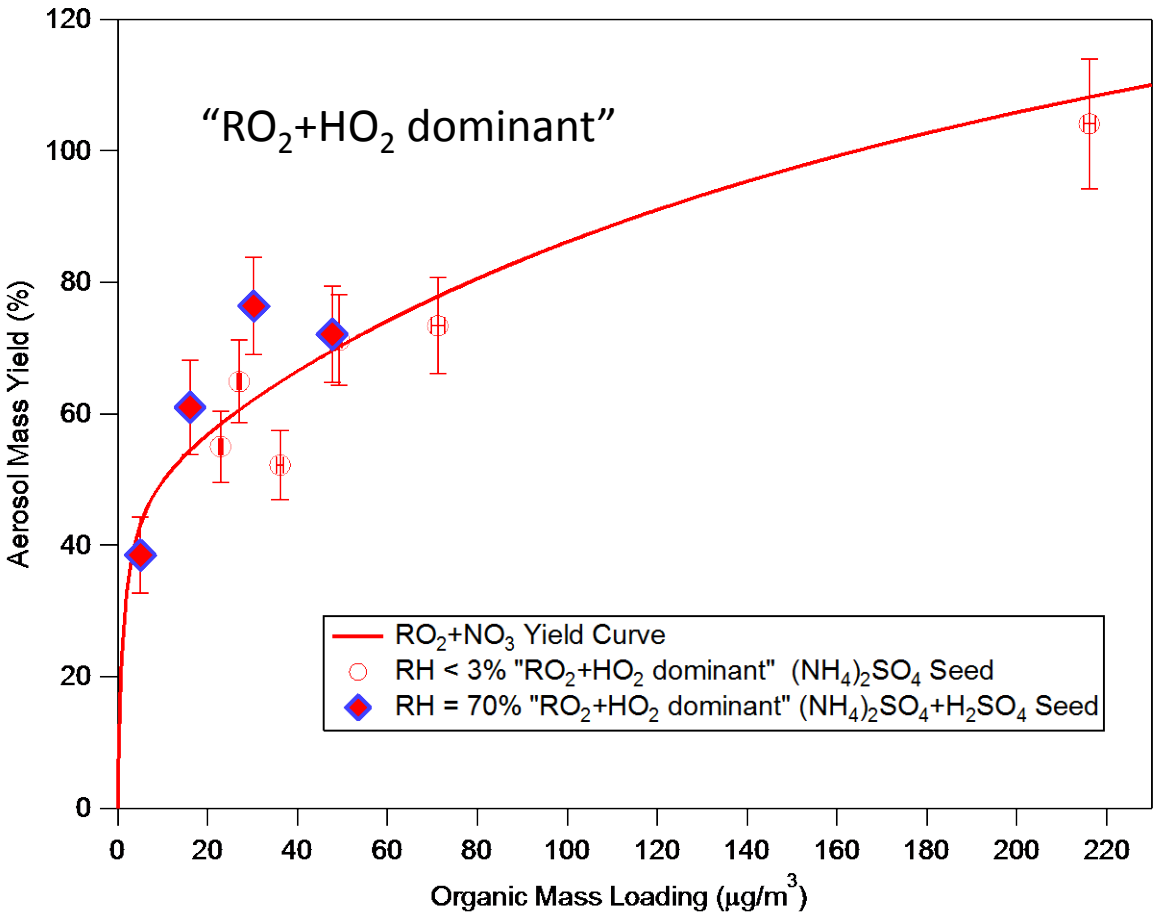


- Highly-oxygenated ON observed in FIGAERO-CIMS with **4 – 9 oxygen atoms**



Nah et al., ES&T, 2016

β-pinene+NO_3: SOA Yields

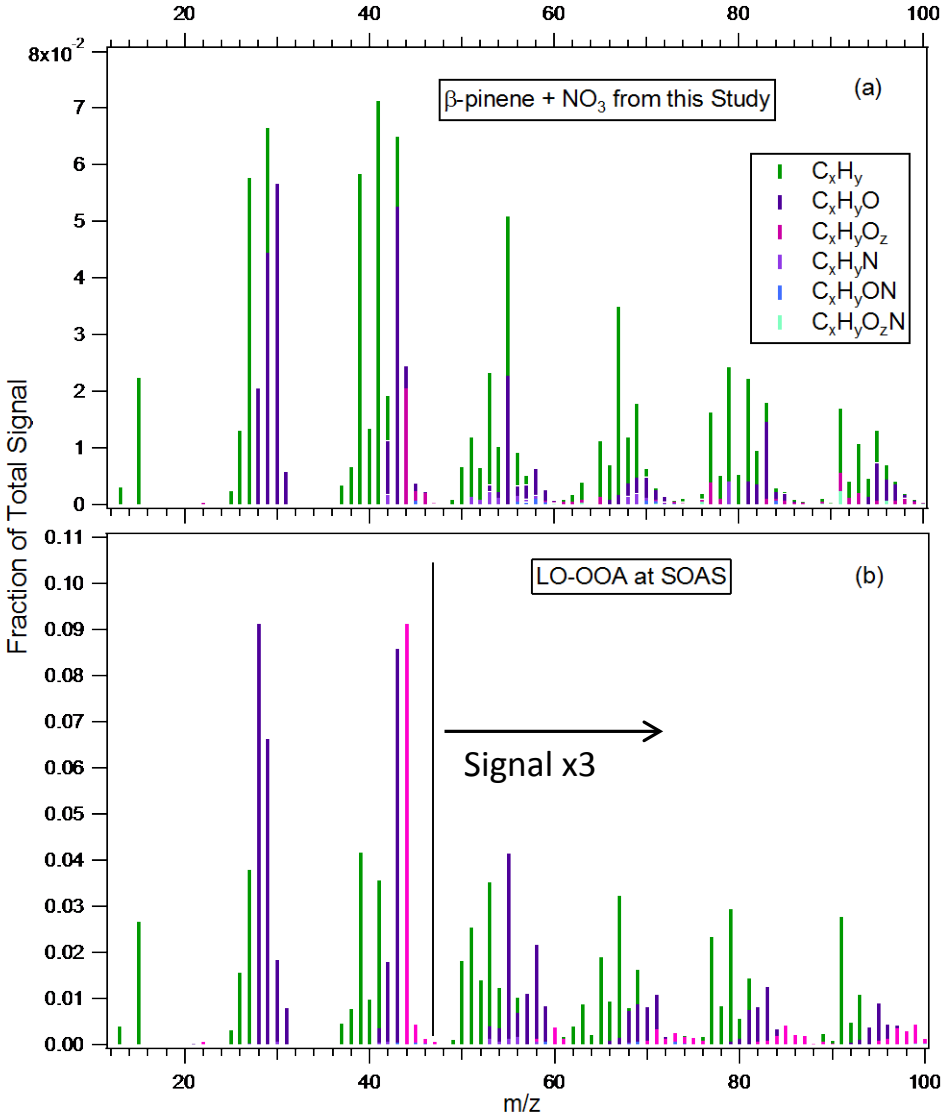


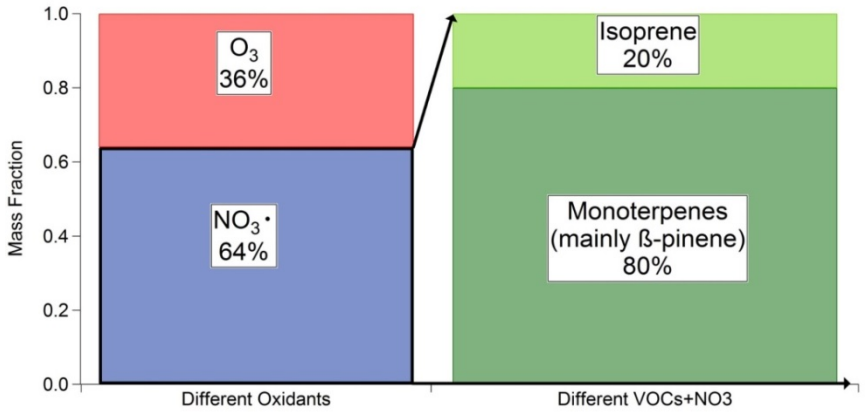
Boyd et al., ACP, 2015

- Humidity and RO_2 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 µg/m^3
- **β-pinene+NO_3 can potentially contribute to a large fraction of ambient aerosol**

Relevance of β-pinene+NO_3 to SOAS

Spectrum of LO-OOA at SOAS has similar features to laboratory β-pinene+NO_3 SOA at *m/z* > 60





Using results from chamber experiments →

β-pinene+NO_3 can potentially make up as much as 50% of nighttime OA production at SOAS

Xu et al., PNAS, 2015
Boyd et al., ACP, 2015

Conclusions

- LO-OOA (19-34%) : likely originates from monoterpenes, and its formation could be controlled by nighttime NO_3 chemistry (NO_x effect)

- Three independent methods to estimate organic nitrate consternations
  - AMS-IC method
  - NO^+/NO_2^+ ratio method (NO_x^+ method)
  - PMF method: include NO^+ and NO_2^+ in PMF analysis

- β-pinene+NO_3 reaction
  - High aerosol mass yields (27.0-104.1%) and particle organic nitrates yields (R_{AN}: 45-74%)
  - This reaction likely contributes substantially to ambient LO-OOA and organic nitrates in the SE US

- Organic nitrates make up a substantial fraction of ambient organic aerosols

Reference

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Ng, N. L., Brown, S. S., Archibald, A. T., Atlas, E., Cohen, R. C., Crowley, J. N., Day, D. A., Donahue, N. M., Fry, J. L., Fuchs, H., Griffin, R. J., Guzman, M. I., Herrmann, H., Hodzic, A., Iinuma, Y., Jimenez, J. L., Kiendler-Scharr, A., Lee, B. H., Luecken, D. J., Mao, J., McLaren, R., Mutzel, A., Osthoff, H. D., Ouyang, B., Picquet-Varrault, B., Platt, U., Pye, H. O. T., Rudich, Y., Schwantes, R. H., Shiraiwa, M., Stutz, J., Thornton, J. A., Tilgner, A., Williams, B. J., and Zaveri, R. A.: Nitrate radicals and biogenic volatile organic compounds: oxidation, mechanisms, and organic aerosol, *Atmos. Chem. Phys.*, 17, 2103-2162, doi:10.5194/acp-17-2103-2017, 2017.

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