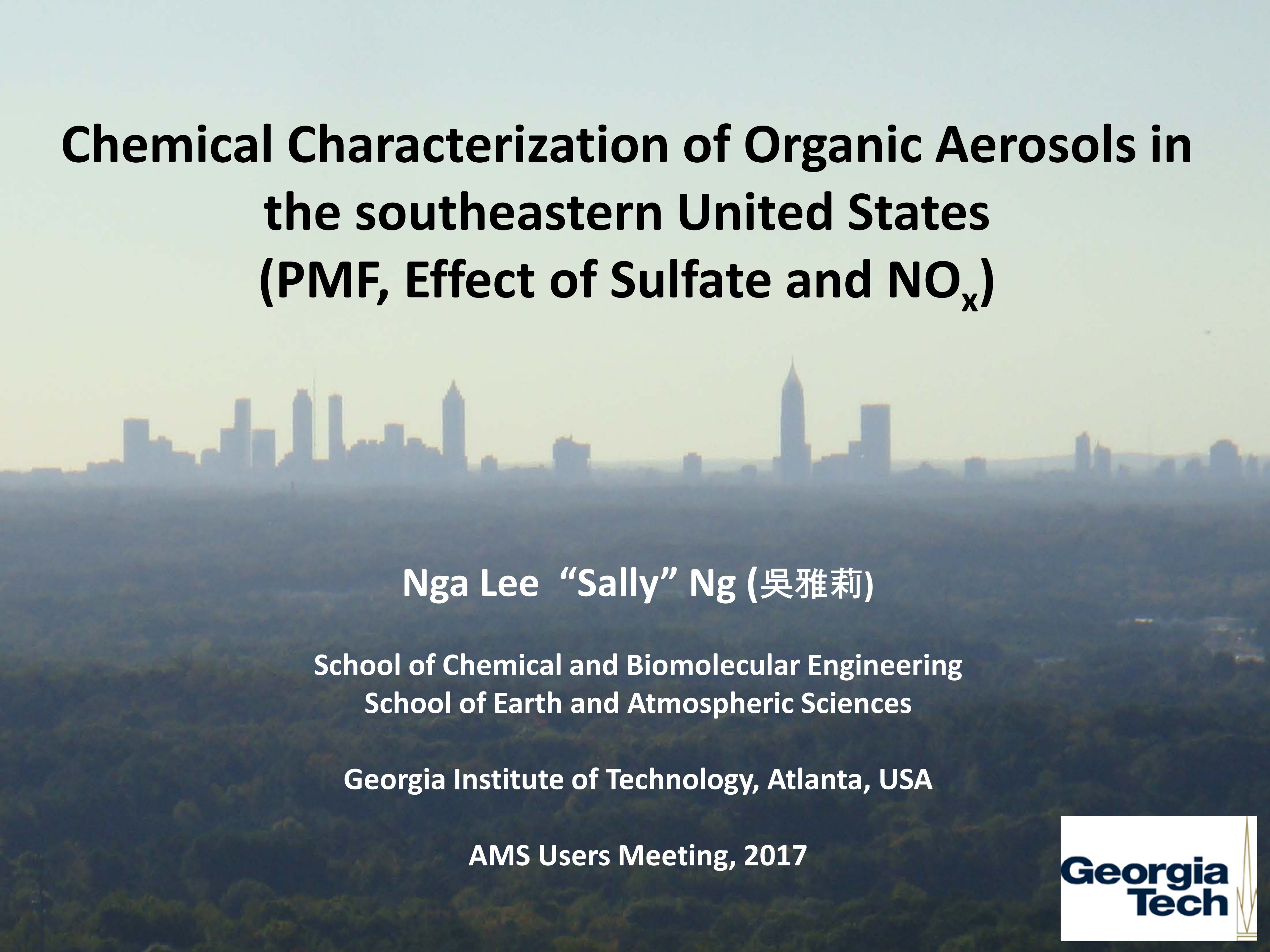

Chemical Characterization of Organic Aerosols in the southeastern United States (PMF, Effect of Sulfate and NO_x)

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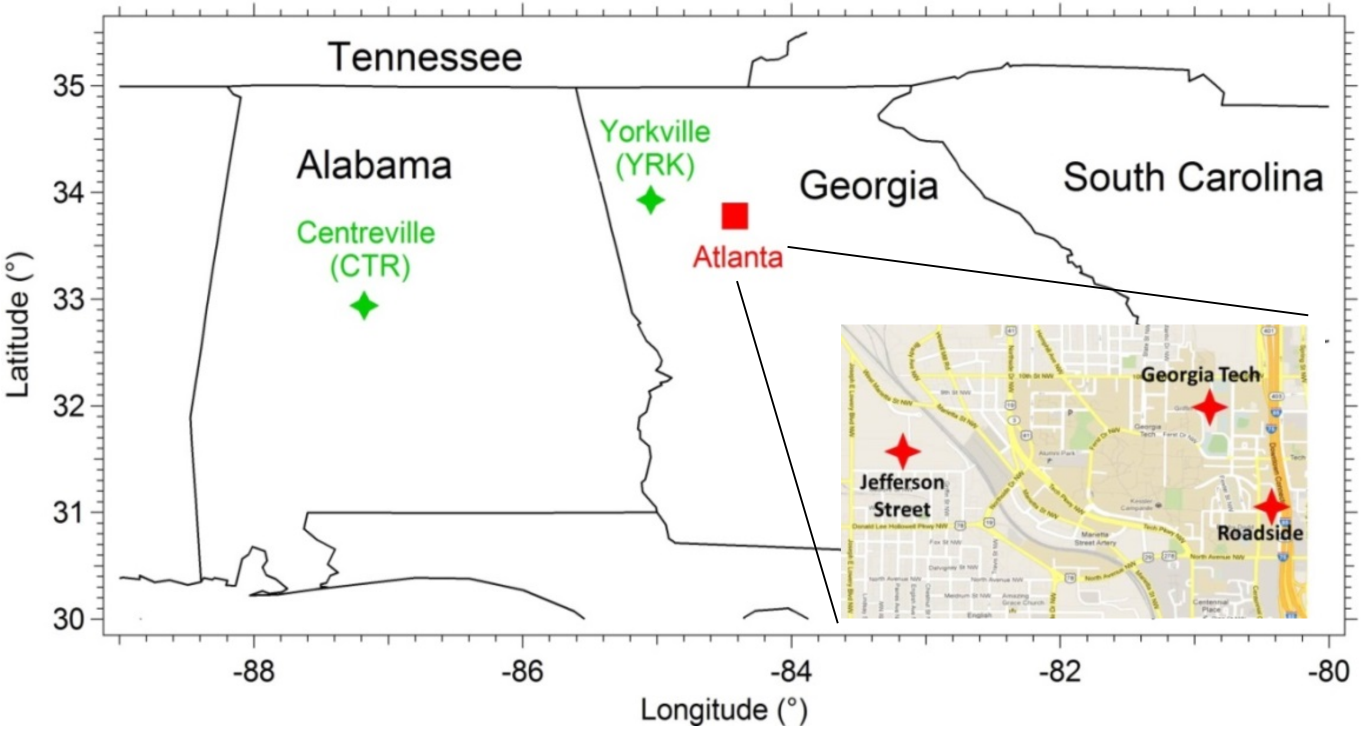
AMS Users Meeting, 2017

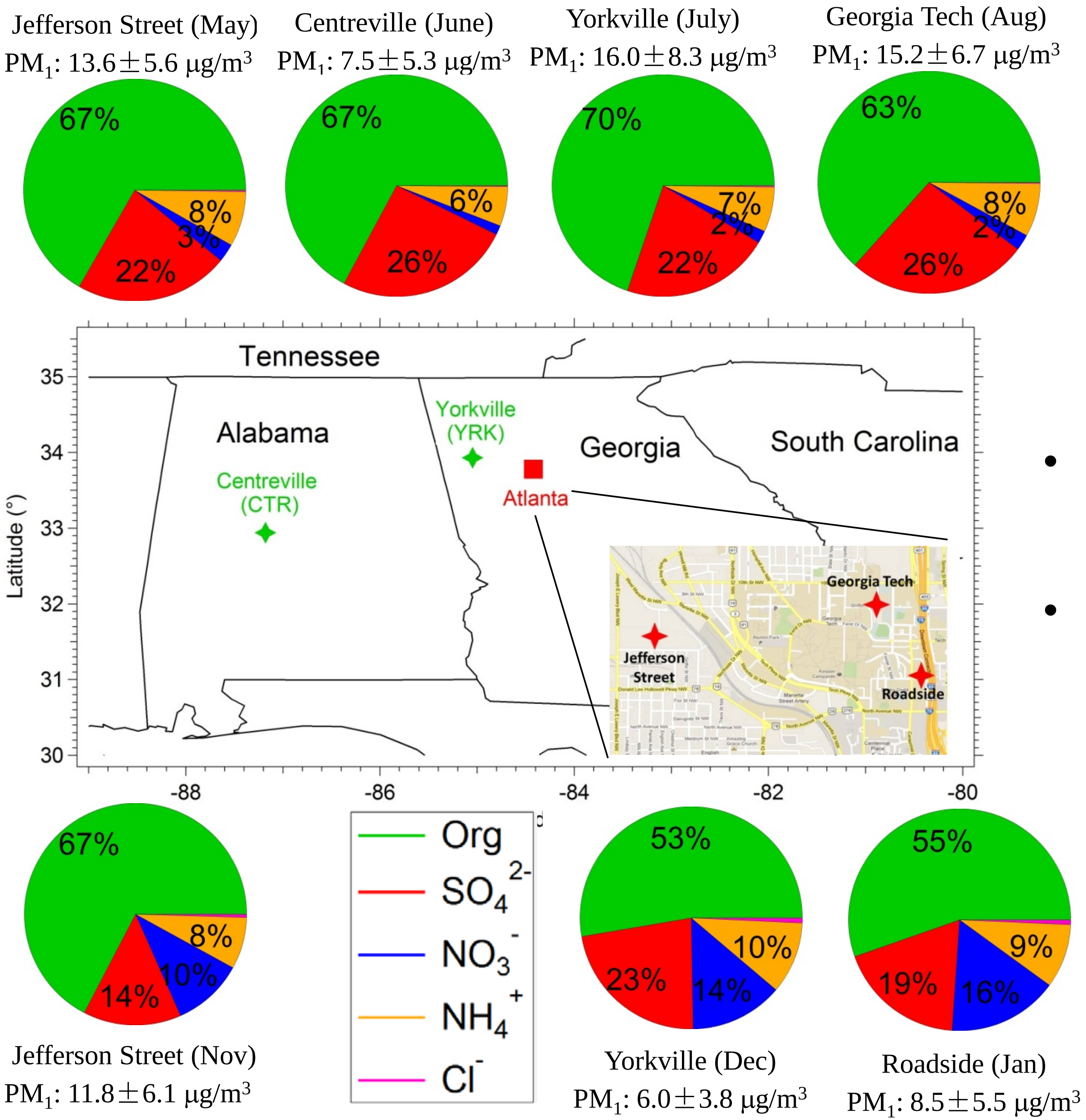
Field Measurements

- **Southern Oxidant and Aerosol Study (SOAS)**
  - 2013 June - July
  - Centreville (rural Alabama)
- **Post-SOAS**
  - 2013 August, Atlanta
- ***Southeast Nexus (SENEX) Study***
  - 2013 June – July
- **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
Xu et al., JGR, 2016
Xu et al., ES&T, 2017

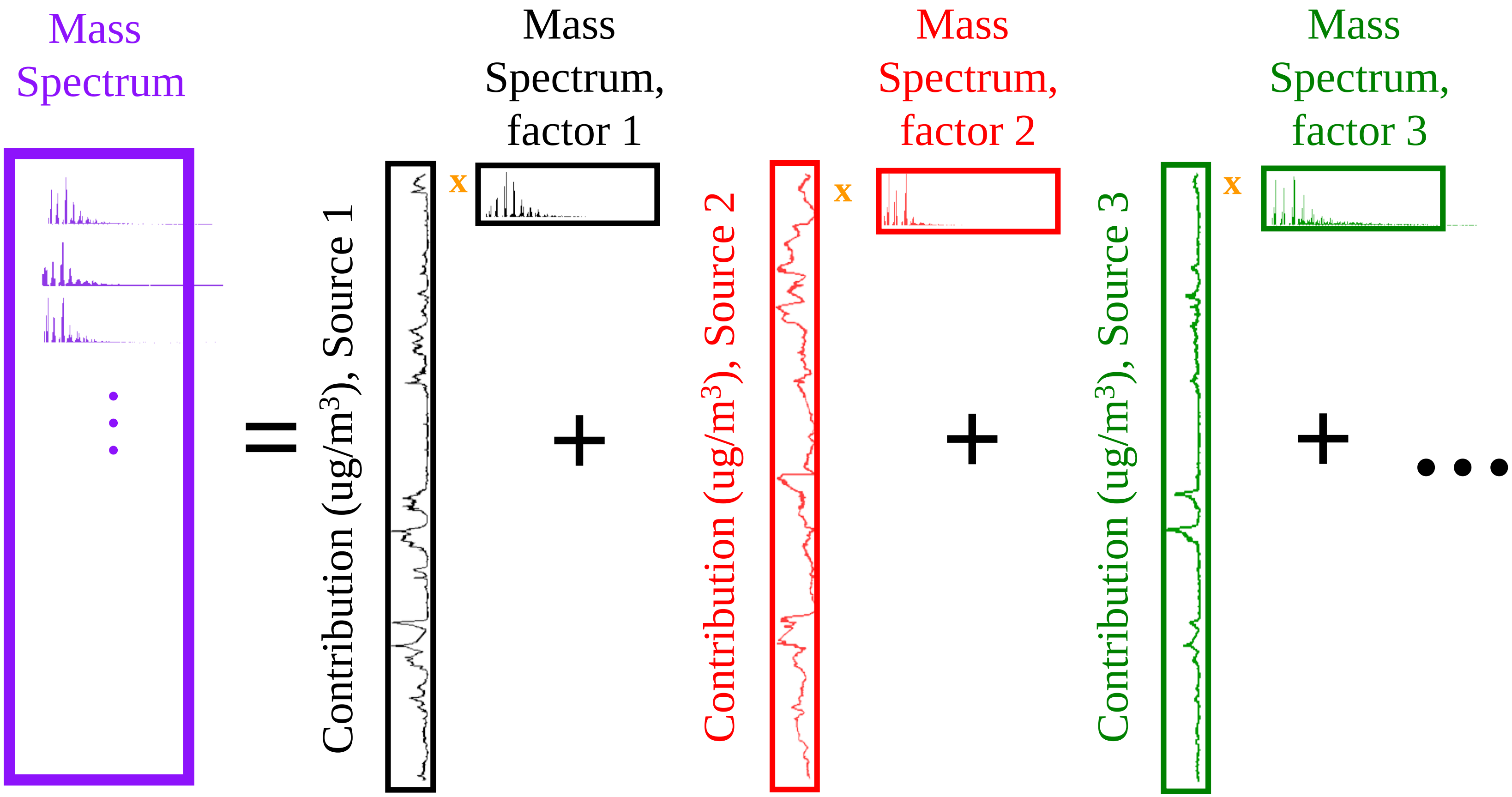
Composition of Ambient Non-refractory PM_1 in SE US



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

Xu et al., PNAS, 2015

Positive Matrix Factorization (PMF) analysis



Mass Spectrum

=

Contribution (ug/m^3), Source 1 x Mass Spectrum, factor 1

+

Contribution (ug/m^3), Source 2 x Mass Spectrum, factor 2

+

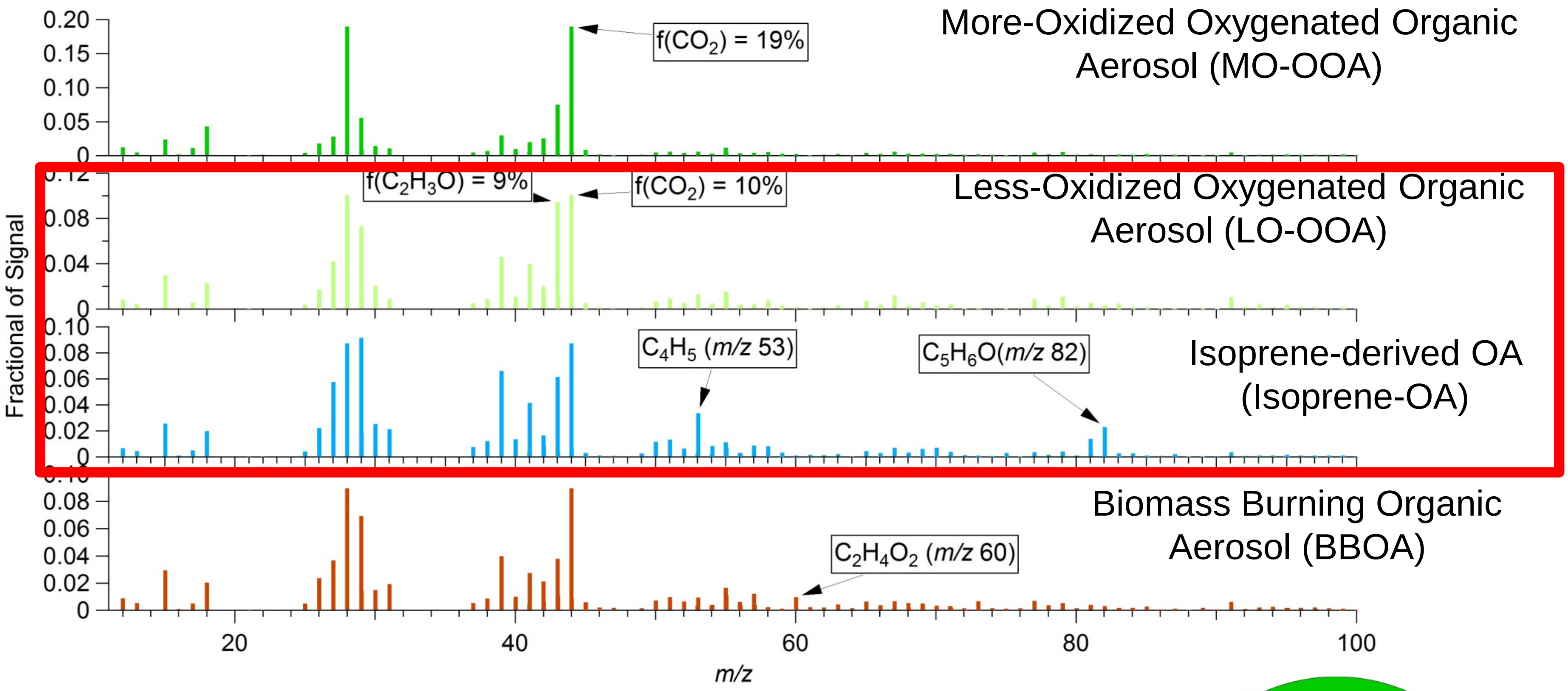
Contribution (ug/m^3), Source 3 x Mass Spectrum, factor 3

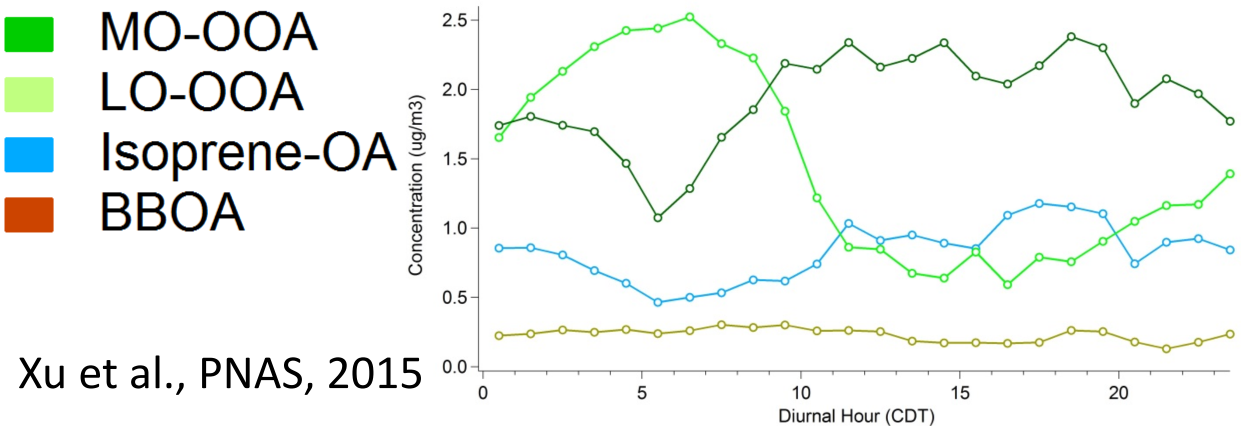
+ …

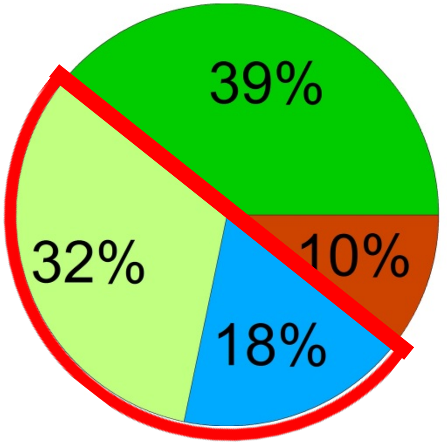
PMF is a bilinear mixing model in which a dataset matrix is assumed to be comprised of the linear combination of factors with constant profiles that have varying contributions across the dataset.

Ulbrich et al. 2009 ACP

Centreville data: PMF results

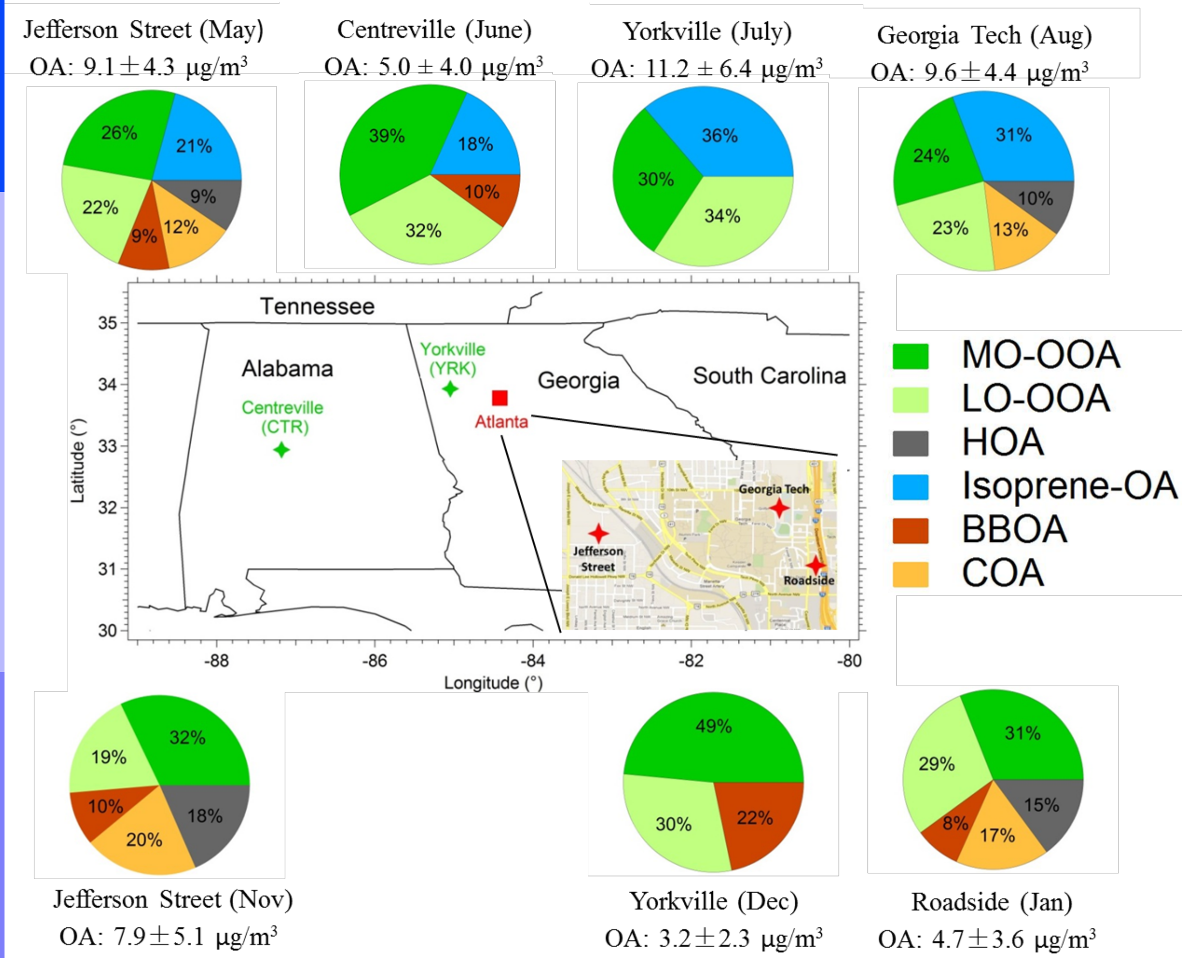






Xu et al., PNAS, 2015

OA Source Apportionment in the SE US



Xu et al., PNAS, 2015

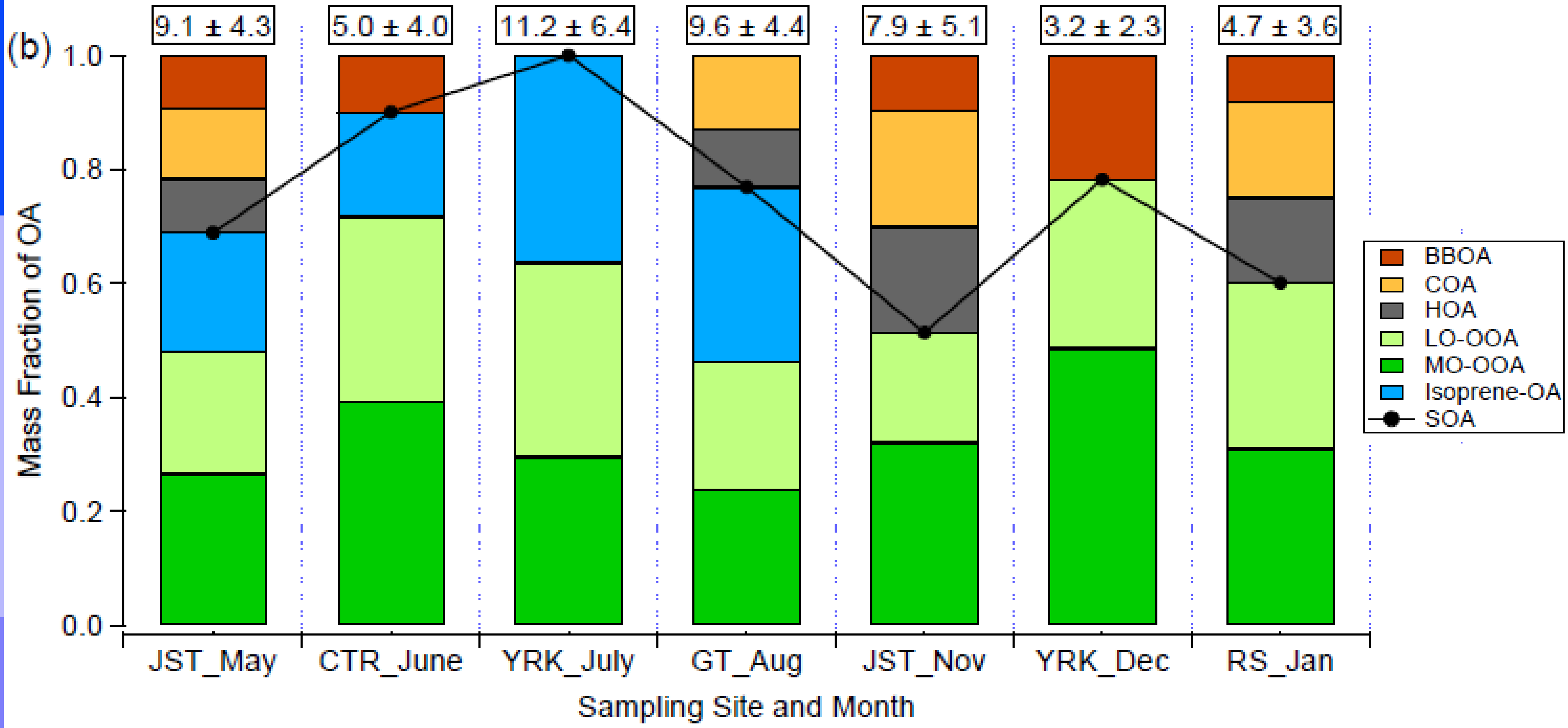
Isoprene-OA only in warmer months, 18 – 36% of total OA

→ Importance of sulfate

Less-Oxidized Oxygenated Organic Aerosol (LO-OOA) important in all seasons, 19-34% of total OA

→ Importance of BVOC+NO_3

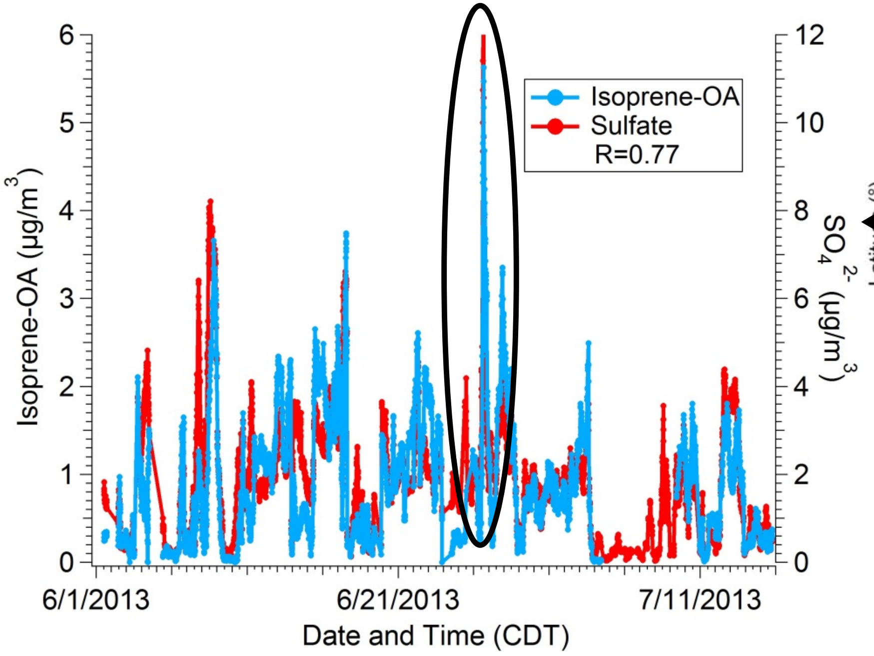
Mass Fraction of Different OA Subtypes



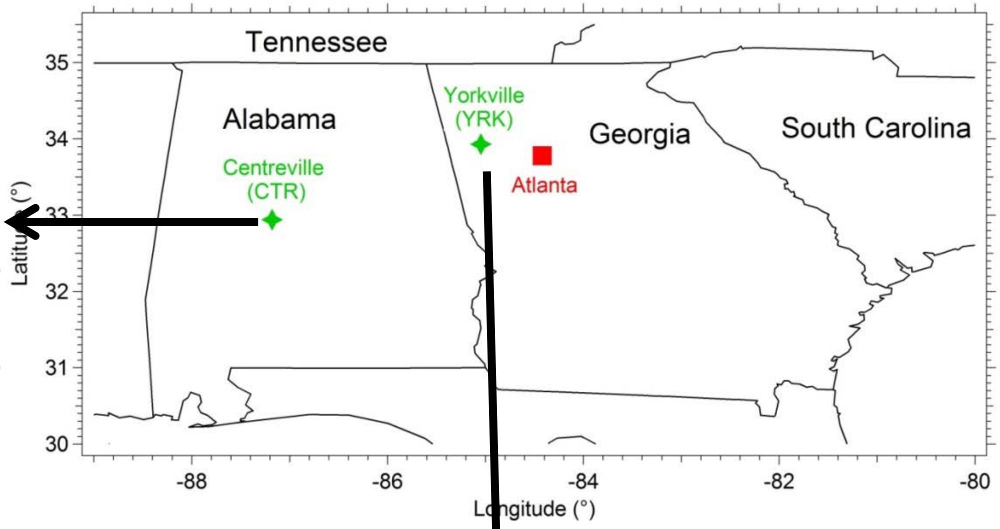
- SOA (Isop_OA, MO-OOA and LO-OOA) dominated OA in summer
- HOA (surrogate for POA) highest at Jefferson Street, Roadside
- BBOA fraction evident in winter and summer

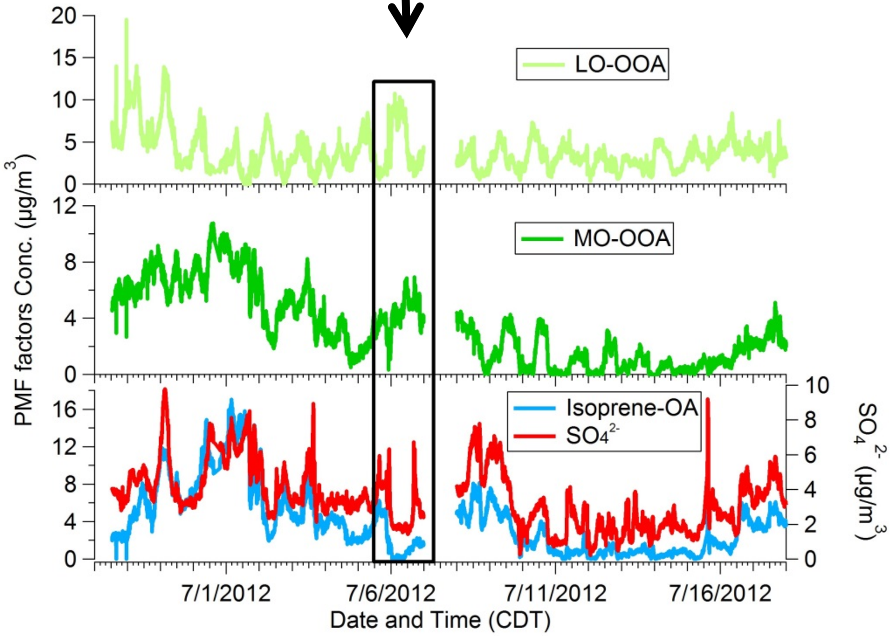
Xu et al., PNAS, 2015
Xu et al., ACP, 2015

Isoprene-OA: Correlation with Sulfate



High SO_4 may enhance "Isoprene-OA" formation

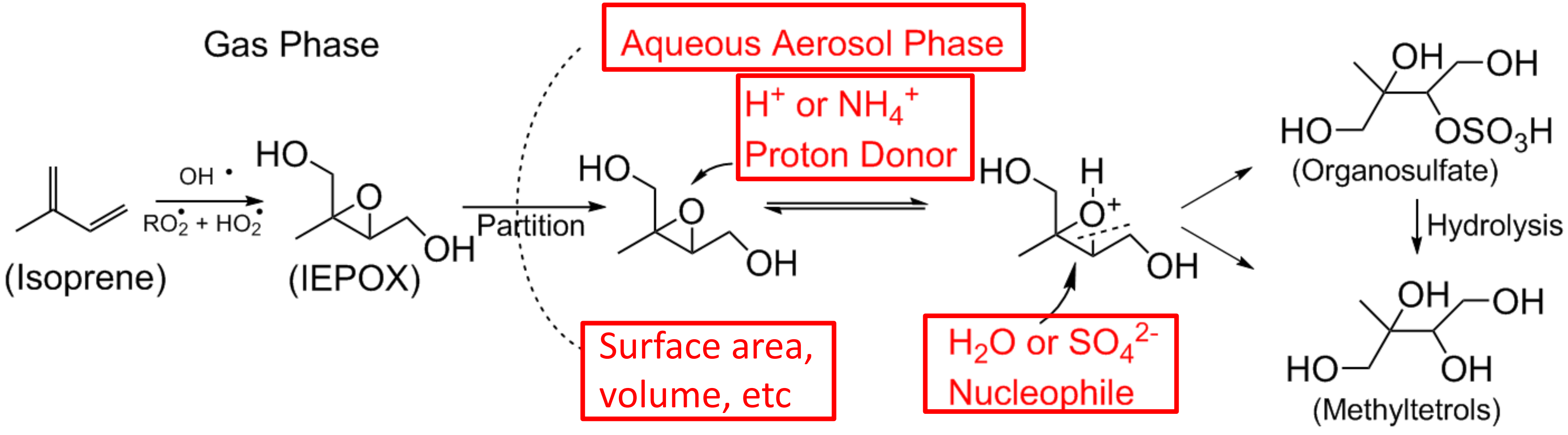




- Isoprene-OA factor has a strong association with sulfate (R between 0.7 and 0.9).
- What's the role of sulfate in Isoprene-OA formation?

Low SO_4 may limit Isoprene-OA formation.

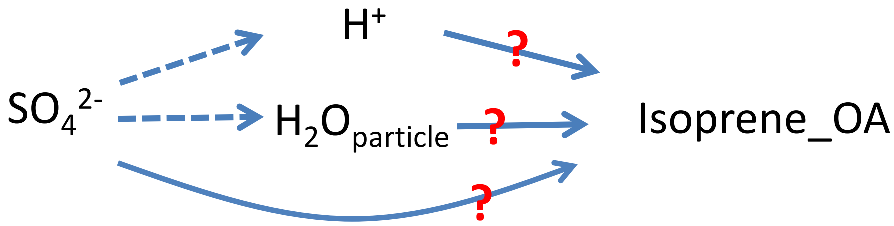
Isoprene-OA: Formation Mechanism



Challenges in determining the role of SO_4:

1) Convoluted interaction between SO_4, particle water and acidity.

2) Determination of particle water and particle acidity (Guo et al., 2015)



Xu et al., PNAS, 2015

Effect of SO4, acidity, and water on Isoprene-OA -- Multivariate Linear Regression

$$\text{Isoprene-OA} = \beta_0 + \beta_1 * H_2O + \beta_2 * [H^+] + \beta_3 * SO_4$$

Adjusted $R^2 = 0.66$

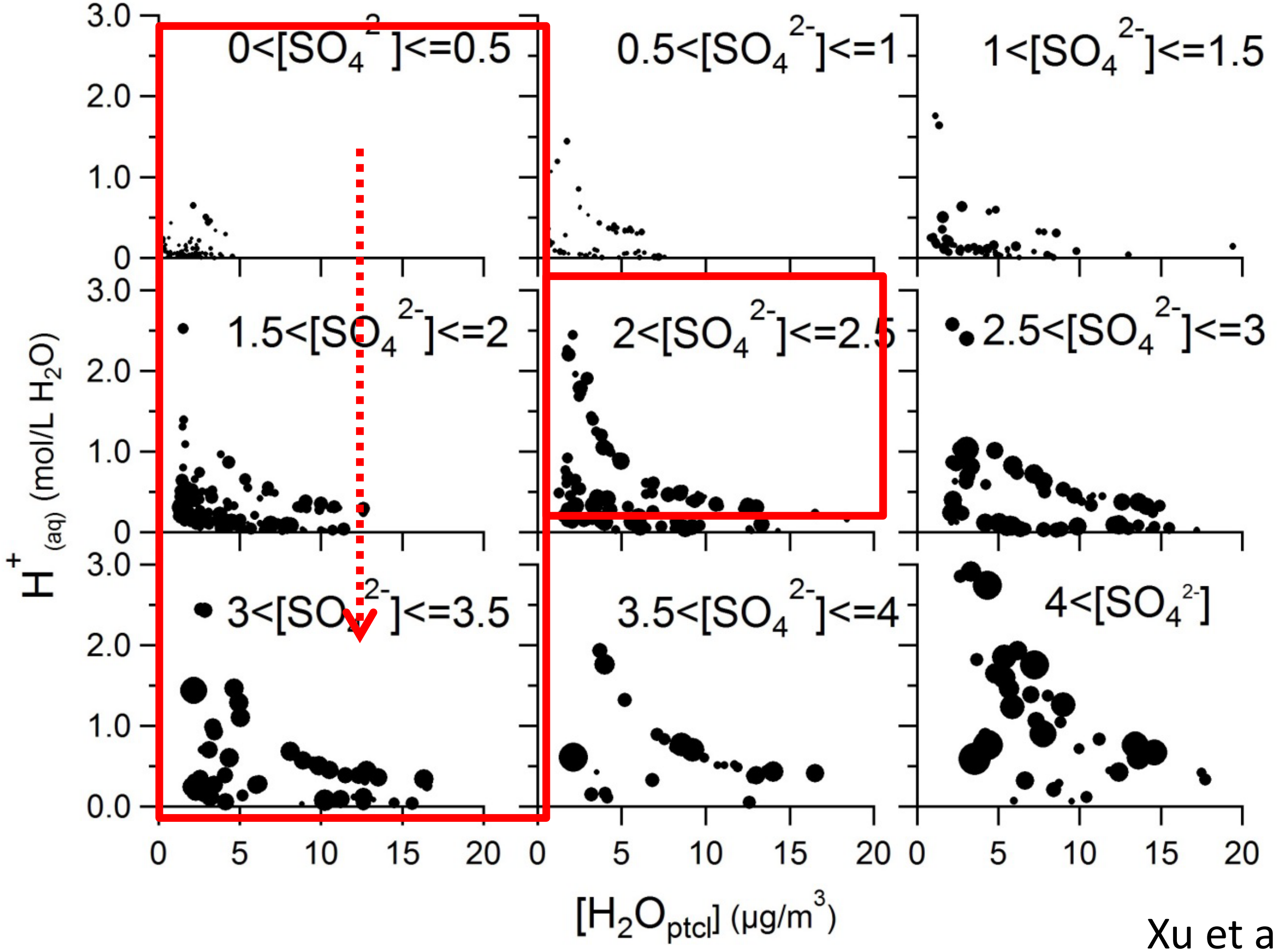
Variable	β-coefficient	Standard error	t Value	P value
Intercept	0.267	0.094	2.82	0.0049
H_2O	-0.004	0.008	-0.50	0.6171
H^+	0.009	0.048	0.18	0.8540
SO_4	0.424	0.022	19.23	<0.0001

- SO_4 has the strongest association with Isoprene-OA (P value < 0.0001)
- Isoprene-OA vs H_2O or acidity → not significant
- It is SO_4, instead of H_2O or acidity, that limits isoprene OA formation

Xu et al., PNAS, 2015

Isoprene-OA: Effect of SO4

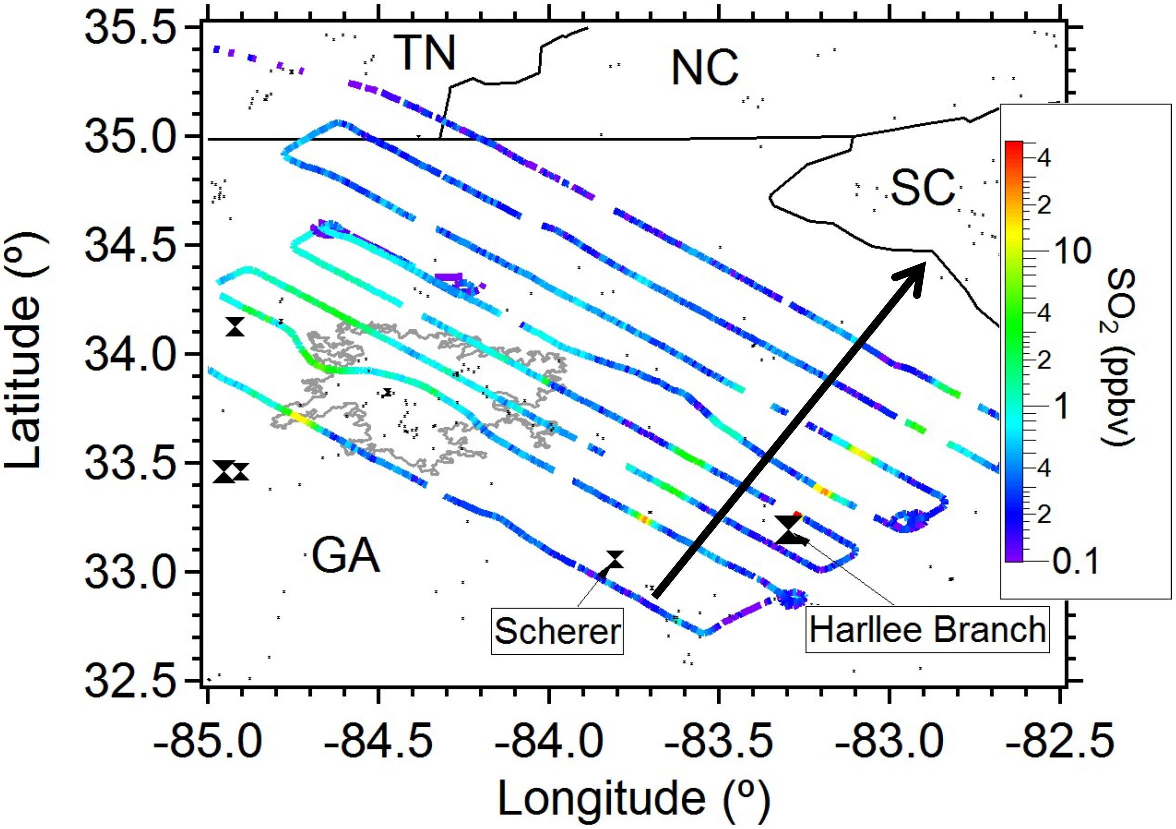
- All data points grouped into nine bins based on 0.5µg/m^3 increment in SO_4 concentration
- Represent isoprene-OA concentration by size of data • 0.5 µg/m^3 ● 1.5 µg/m^3 ● 2.5 µg/m^3 ⬤ 3.5 µg/m^3

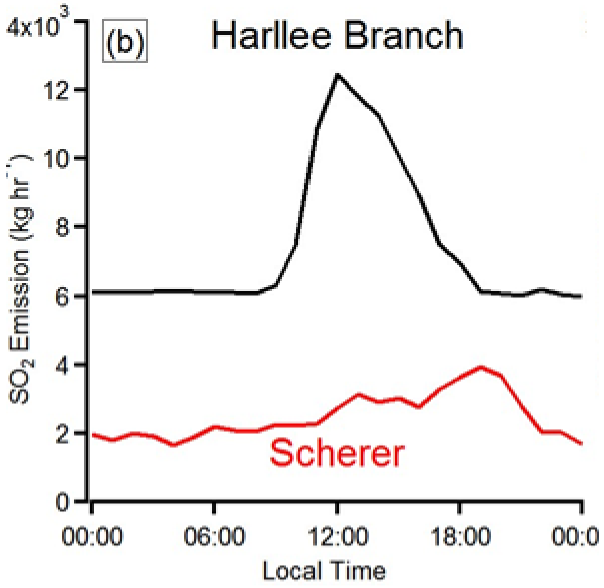


Xu et al., PNAS, 2015

Southeast Nexus (SENEX) Study

AMS data from
Ann Middlebrook (NOAA)

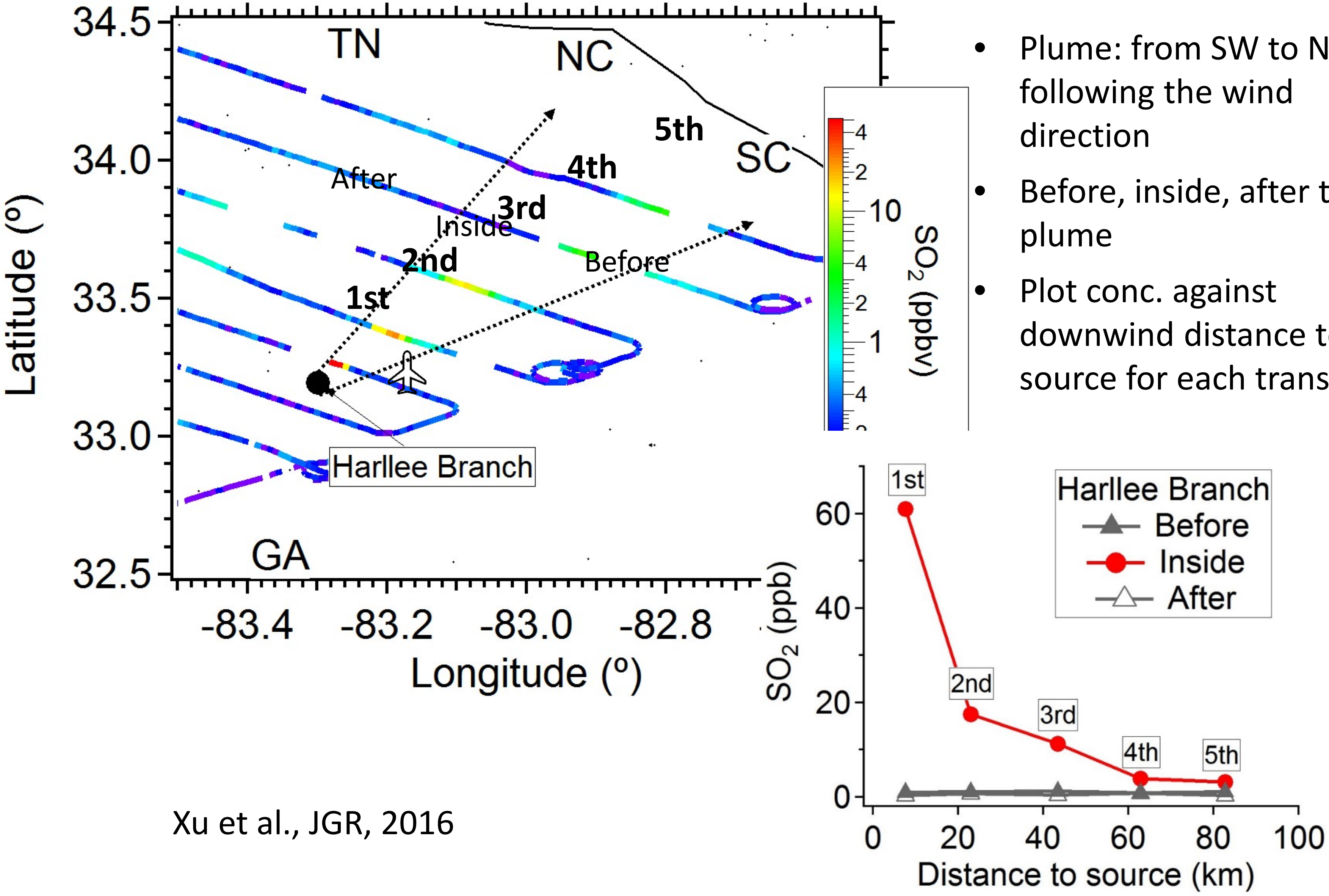




- Flight June 16th: Over Georgia. Wind direction: mainly SW
- Focus on two power plants: Scherer and Harllee Branch
  → sample downwind of power plant (e.g. high SO_2).

Xu et al., JGR, 2016

Plume Evolution

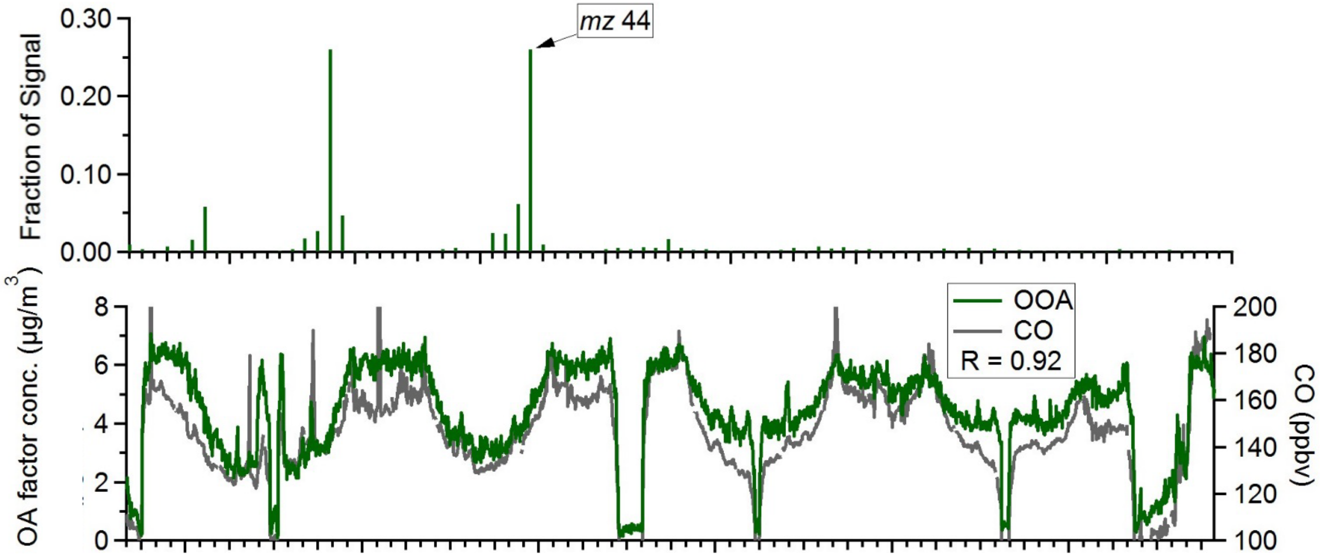


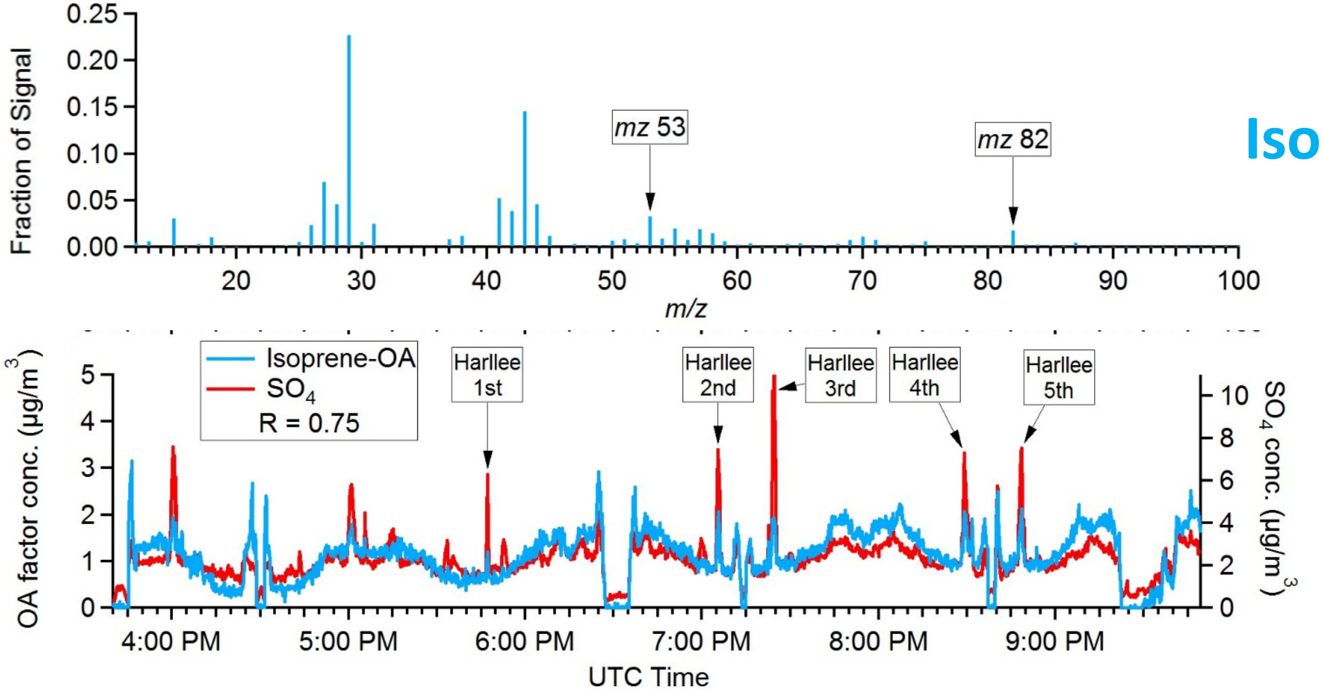
- Plume: from SW to NE following the wind direction
- Before, inside, after the plume
- Plot conc. against downwind distance to source for each transect.

Xu et al., JGR, 2016

Positive Matrix Factorization (PMF) Results

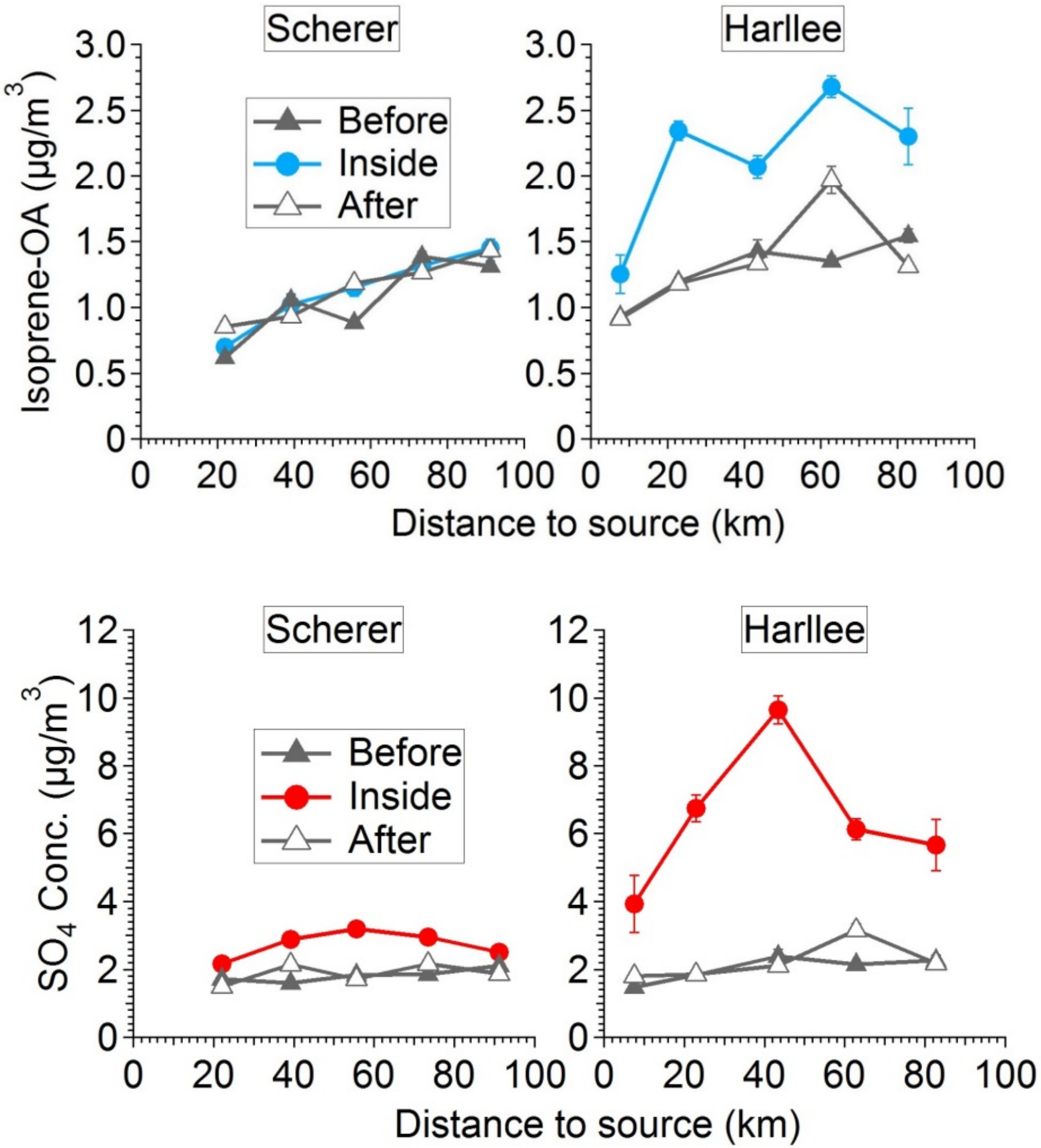
Oxygenated OA (OOA)





Isoprene-derived OA (Isop-OA)

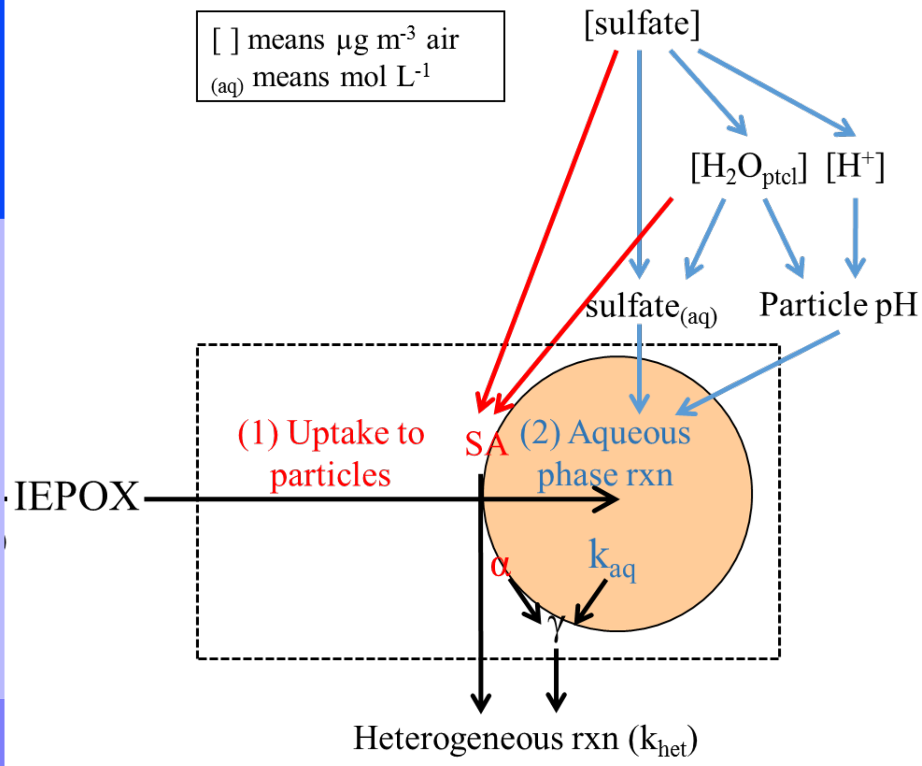
Evolution of Isoprene-OA and Sulfate



- Isoprene-OA is enhanced in Harllee Branch, but not in Scherer.
- Consistent with substantial sulfate enhancement in Harllee, but not in Scherer.
- What's the role of sulfate in isoprene-OA formation?

Xu et al., JGR, 2016

Isoprene-OA vs SO_4/acidity/water



[ ] means µg m^{-3} air
(aq) means mol L^{-1}

[sulfate]

$[H_2O_{ptcl}]$ $[H^+]$

$sulfate_{(aq)}$

Particle pH

(1) Uptake to particles

SA

(2) Aqueous phase rxn

IEPOX

α

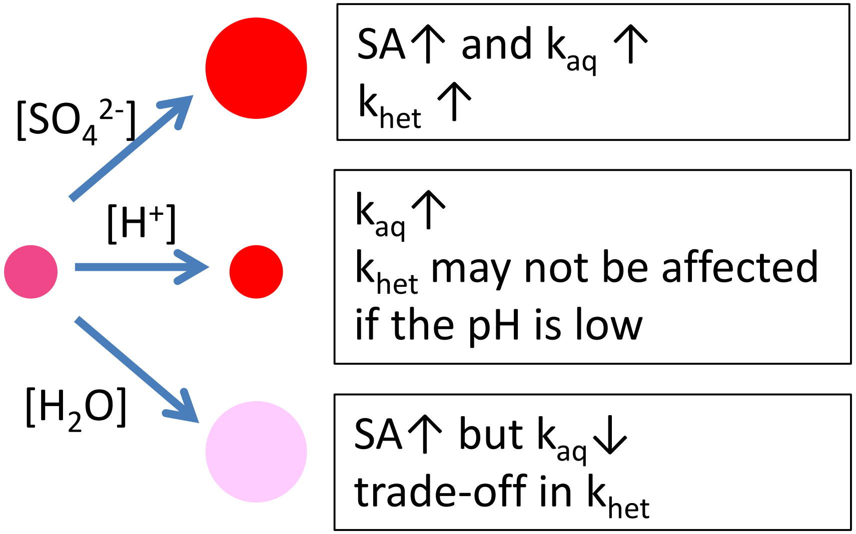
k_{aq}

γ

Heterogeneous rxn (k_{het})

$$k_{het} = \frac{\gamma \upsilon S_a}{4}$$

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{\nu}{4H_{IEPOX}RT\sqrt{D_a k_{aq}}}\frac{1}{f(q)}$$



$[SO_4^{2-}]$

SA↑ and k_{aq} ↑
k_{het} ↑

$[H^+]$

k_{aq}↑
k_{het} may not be affected if the pH is low

$[H_2O]$

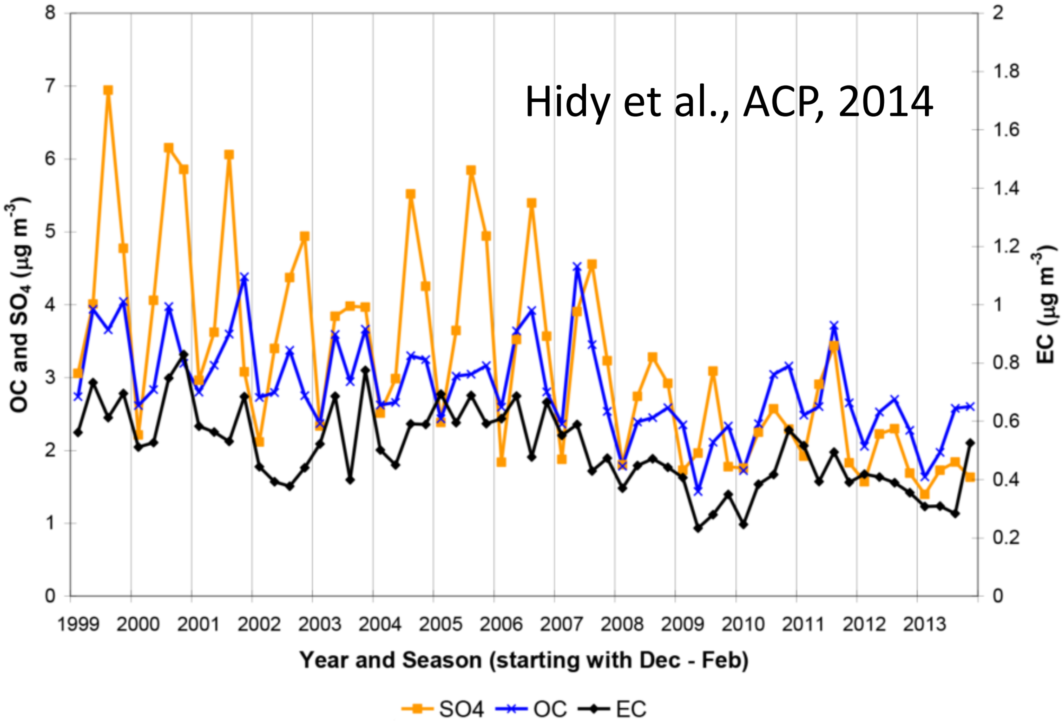
SA↑ but k_{aq}↓
trade-off in k_{het}

- Competition between 1) IEPOX uptake to particles and 2) subsequent aqueous-phase reactions
- Sulfate enhances both steps. High particle acidity. Trade-off effects of particle water.

Magnitude of Sulfate Effect on Isoprene-OA

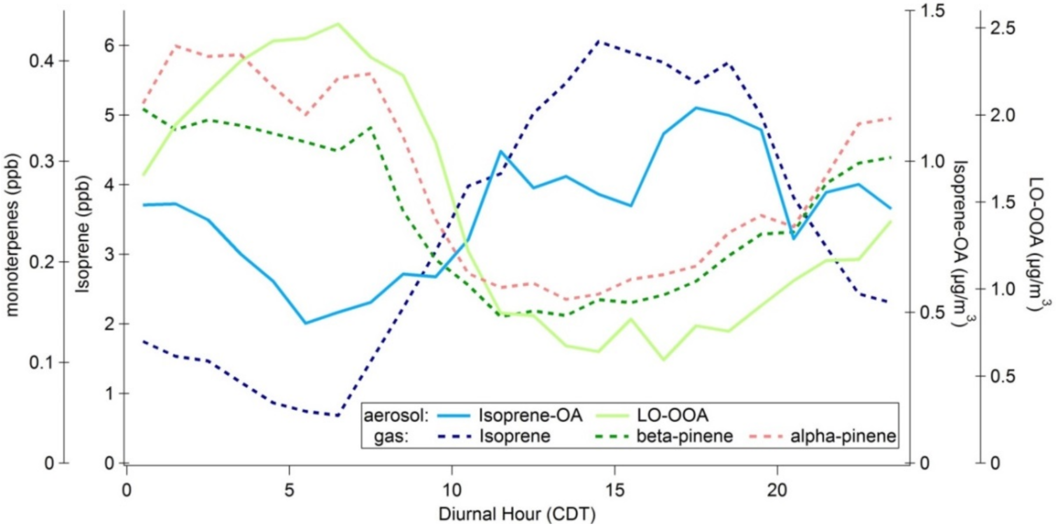
Reduction in isoprene-OA associated with 1 $\mu g/m^3$ reduction in sulfate.

	Reduction in OA ($\mu g/m^3$)	Method
Xu et al., PNAS, 2015	0.42	SOAS ground measurement
Xu et al., JGR, 2016	0.23	SENEX airborne measurement
Blanchard et al., ACP, 2015	0.35	Stats analysis on 15 years data in SE

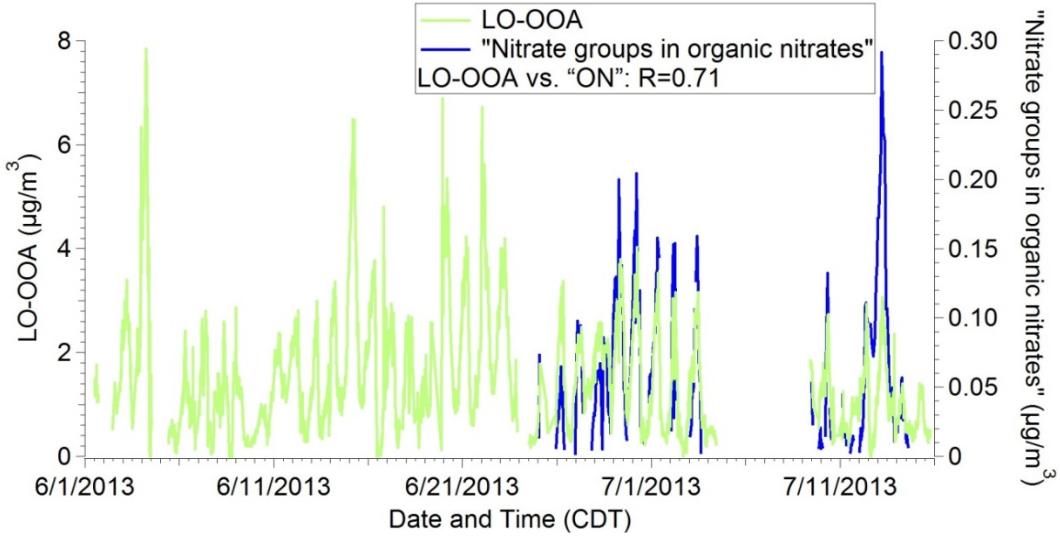

Hidy et al., ACP, 2014

Roughly 30% of the total OA reduction could possibly arise from the sulfate control over isoprene-OA formation

LO-OOA at SOAS (see Monday’s presentation for details)



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



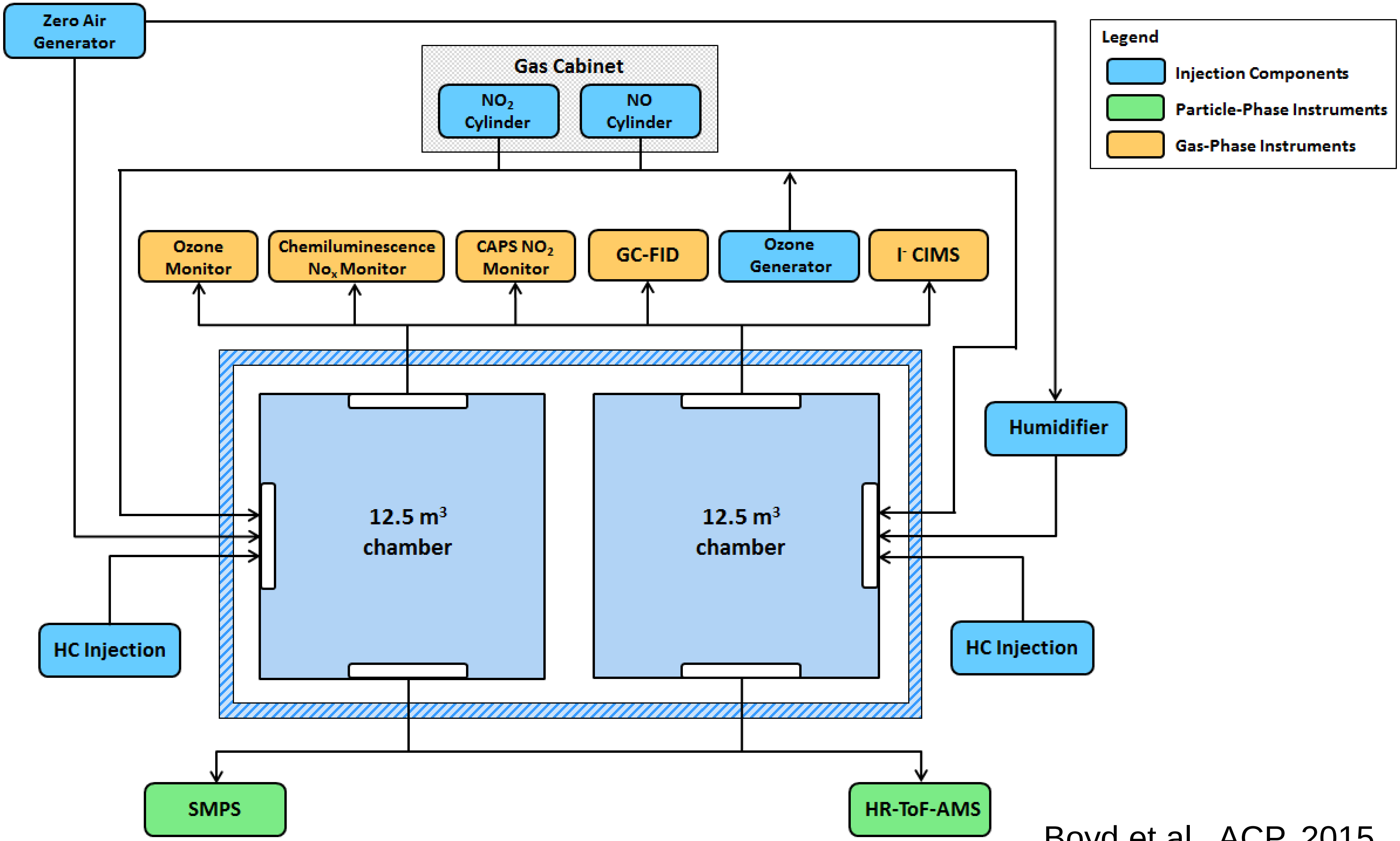
- LO-OOA is strongly correlated with “nitrate groups (-ONO2) in organic nitrates”
- Estimated based on AMS-IC method

Contribution of monoterpenes + $NO_3^{\bullet}$ chemistry to LO-OOA

Xu et al., PNAS, 2015

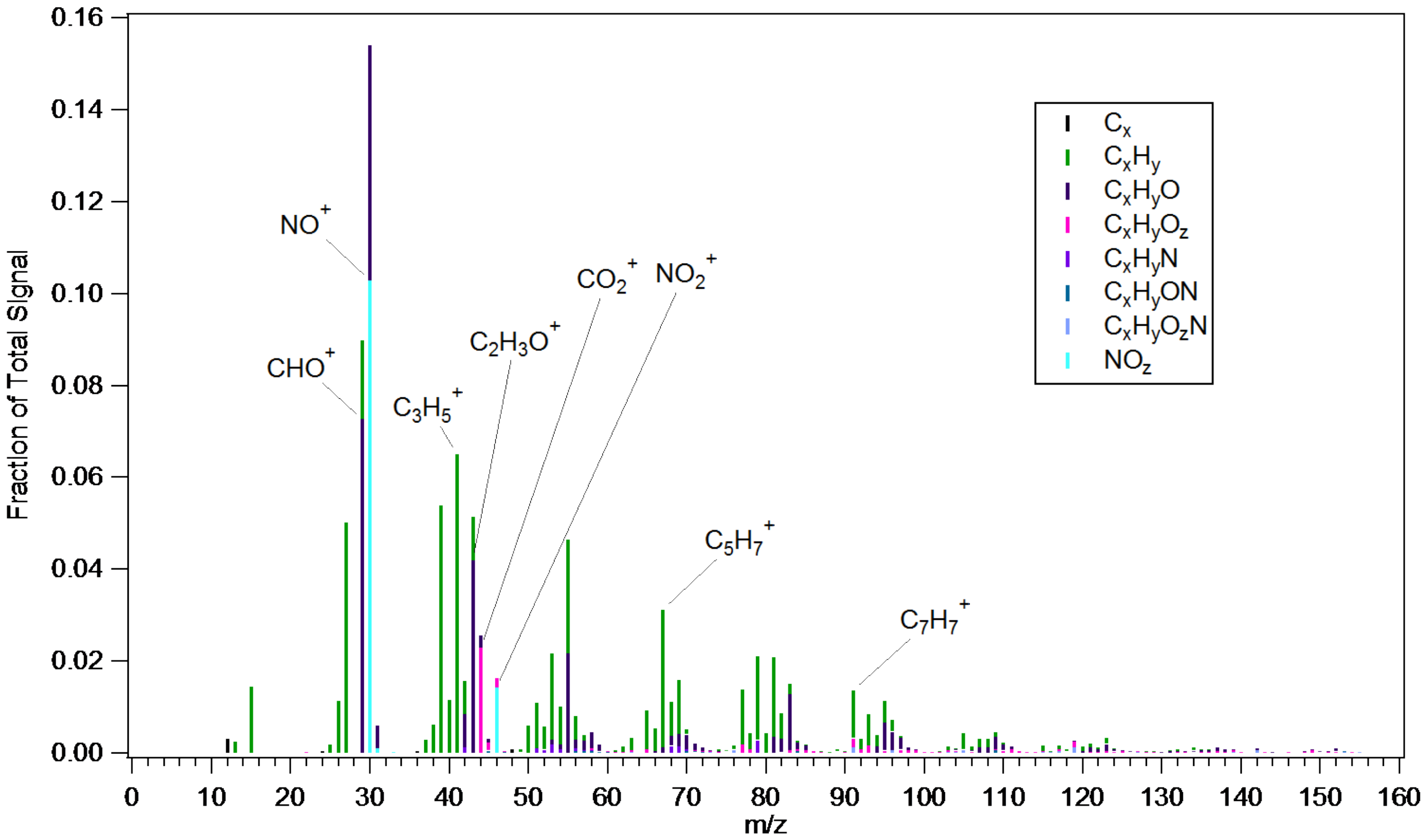
Georgia Tech Environmental Chamber Facility

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



Boyd et al., ACP, 2015

β-pinene+NO_3: Aerosol Composition

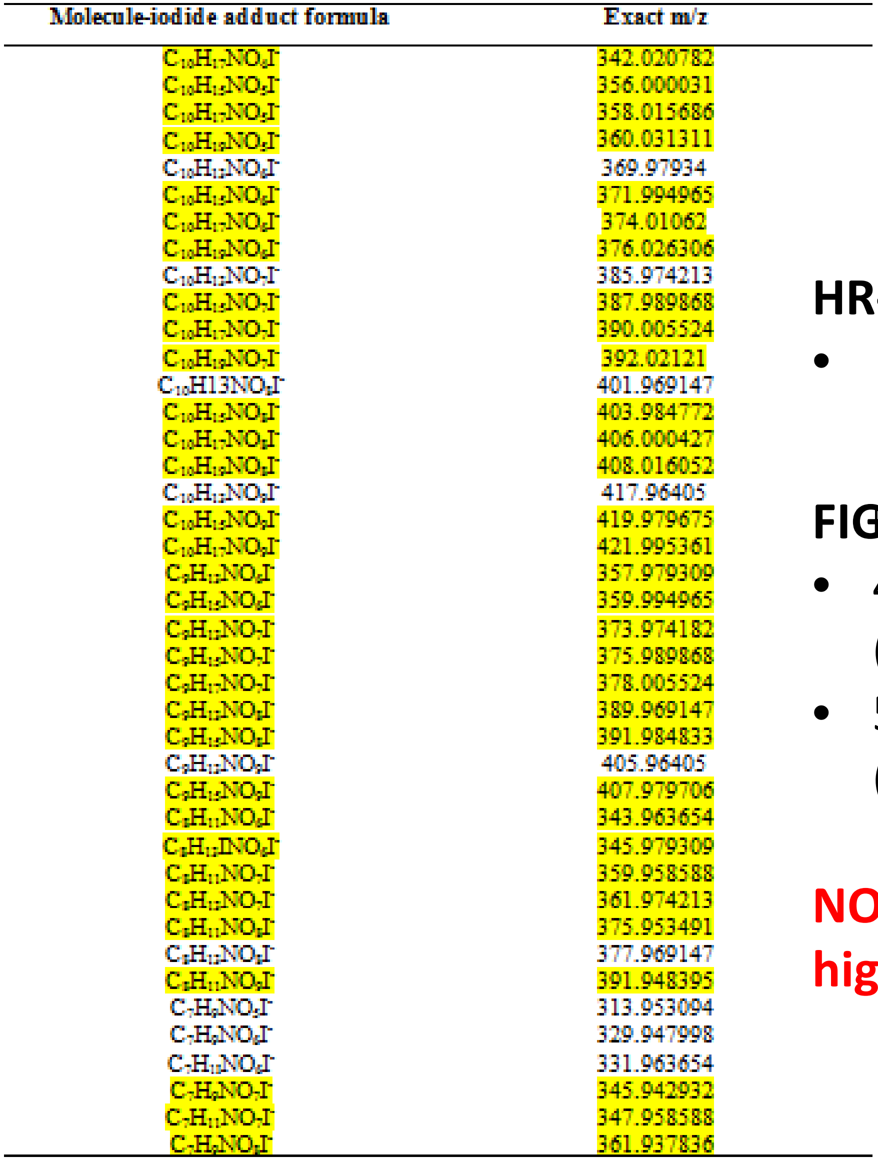


- Large fraction of nitrate species at NO^+ (*m/z* 30) and NO_2^+ (*m/z* 46)
  - Estimated that 45-74% of aerosol is composed of organic nitrates
- Relatively large signal at m/z 67 ($C_5H_7^+$) and m/z 91 ($C_7H_7^+$)

Boyd et al., ACP, 2015

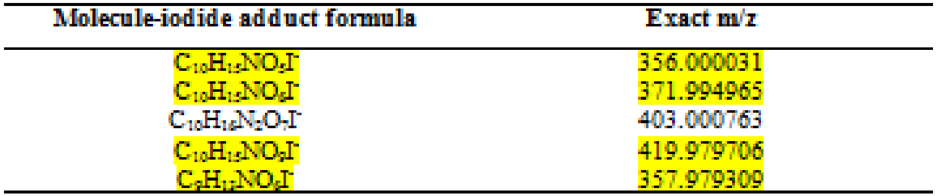
Bulk and Speciated Organic Nitrates

β-pinene + NO_3



Molecule-iodide adduct formula	Exact m/z
$C_{10}H_{17}NO_4I^-$	342.020782
$C_{10}H_{15}NO_5I^-$	356.000031
$C_{10}H_{17}NO_5I^-$	358.015686
$C_{10}H_{19}NO_5I^-$	360.031311
$C_{10}H_{13}NO_6I^-$	369.97934
$C_{10}H_{15}NO_6I^-$	371.994965
$C_{10}H_{17}NO_6I^-$	374.01062
$C_{10}H_{19}NO_6I^-$	376.026306
$C_{10}H_{13}NO_7I^-$	385.974213
$C_{10}H_{15}NO_7I^-$	387.989868
$C_{10}H_{17}NO_7I^-$	390.005524
$C_{10}H_{19}NO_7I^-$	392.02121
$C_{10}H13NO_8I^-$	401.969147
$C_{10}H_{15}NO_8I^-$	403.984772
$C_{10}H_{17}NO_8I^-$	406.000427
$C_{10}H_{19}NO_8I^-$	408.016052
$C_{10}H_{13}NO_9I^-$	417.96405
$C_{10}H_{15}NO_9I^-$	419.979675
$C_{10}H_{17}NO_9I^-$	421.995361
$C_9H_{13}NO_6I^-$	357.979309
$C_9H_{15}NO_6I^-$	359.994965
$C_9H_{13}NO_7I^-$	373.974182
$C_9H_{15}NO_7I^-$	375.989868
$C_9H_{17}NO_7I^-$	378.005524
$C_9H_{13}NO_8I^-$	389.969147
$C_9H_{15}NO_8I^-$	391.984833
$C_9H_{13}NO_9I^-$	405.96405
$C_9H_{15}NO_9I^-$	407.979706
$C_8H_{11}NO_6I^-$	343.963654
$C_8H_{13}INO_6I^-$	345.979309
$C_8H_{11}NO_7I^-$	359.958588
$C_8H_{13}NO_7I^-$	361.974213
$C_8H_{11}NO_8I^-$	375.953491
$C_8H_{13}NO_8I^-$	377.969147
$C_8H_{11}NO_9I^-$	391.948395
$C_7H_9NO_5I^-$	313.953094
$C_7H_9NO_6I^-$	329.947998
$C_7H_{11}NO_6I^-$	331.963654
$C_7H_9NO_7I^-$	345.942932
$C_7H_{11}NO_7I^-$	347.958588
$C_7H_9NO_8I^-$	361.937836

α-pinene + NO_3



Molecule-iodide adduct formula	Exact m/z
$C_{10}H_{15}NO_5I^-$	356.000031
$C_{10}H_{15}NO_6I^-$	371.994965
$C_{10}H_{16}N_2O_7I^-$	403.000763
$C_{10}H_{15}NO_9I^-$	419.979706
$C_9H_{13}NO_6I^-$	357.979309

HR-ToF-AMS

- 60-80% of OA is organic nitrates

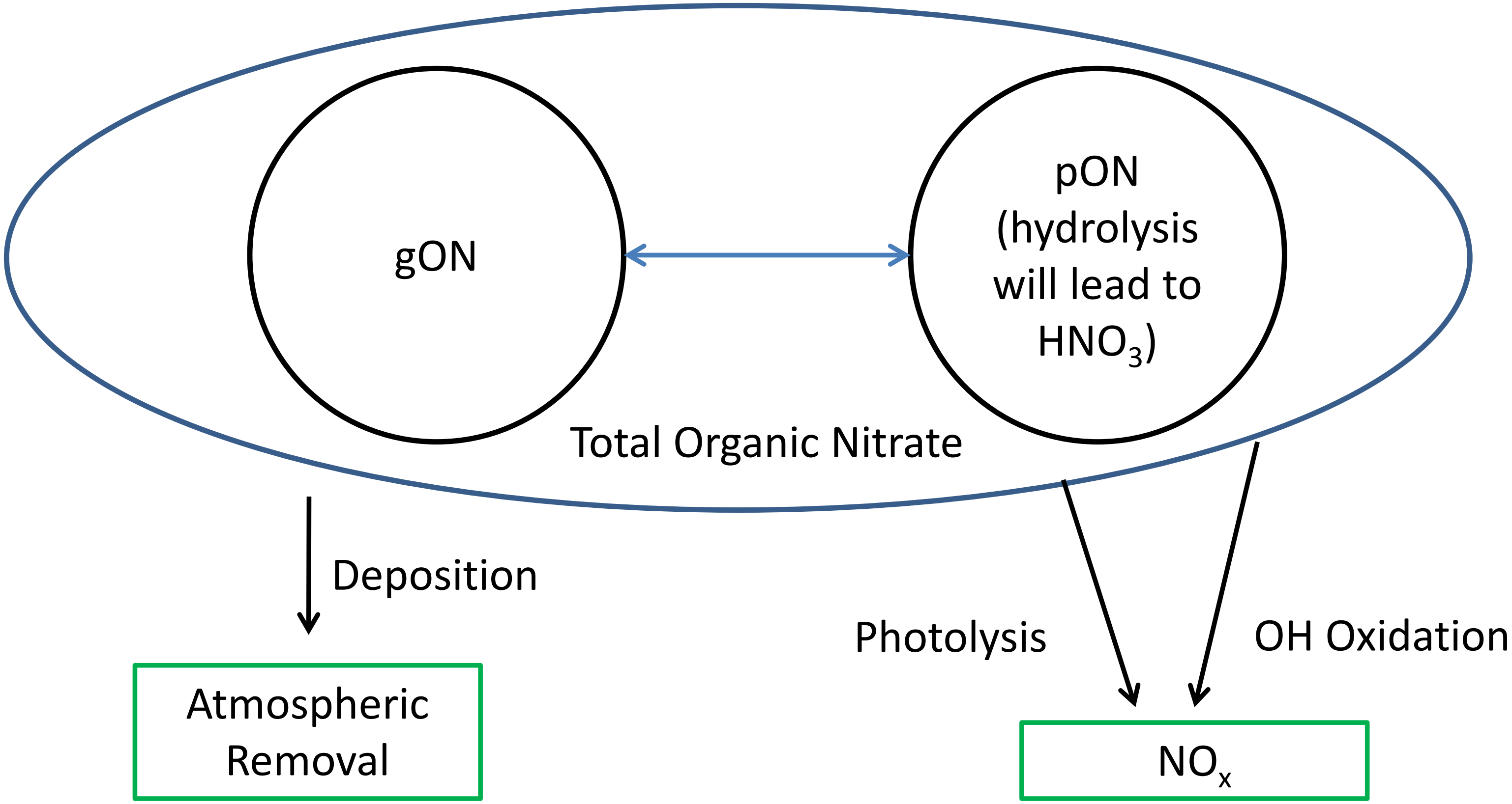
FIGAERO-HR-ToF-CIMS (I^-)

- 41 ON observed for β-pinene+NO_3 (32 observed at SOAS, Lee et al., 2016)
- 5 ON for α-pinene+NO_3 (4 observed at SOAS, Lee et al., 2016)

NO_3 chemistry forms atmospherically relevant highly oxygenated ON

Boyd et al., 2015; Nah et al., ES&T, 2016

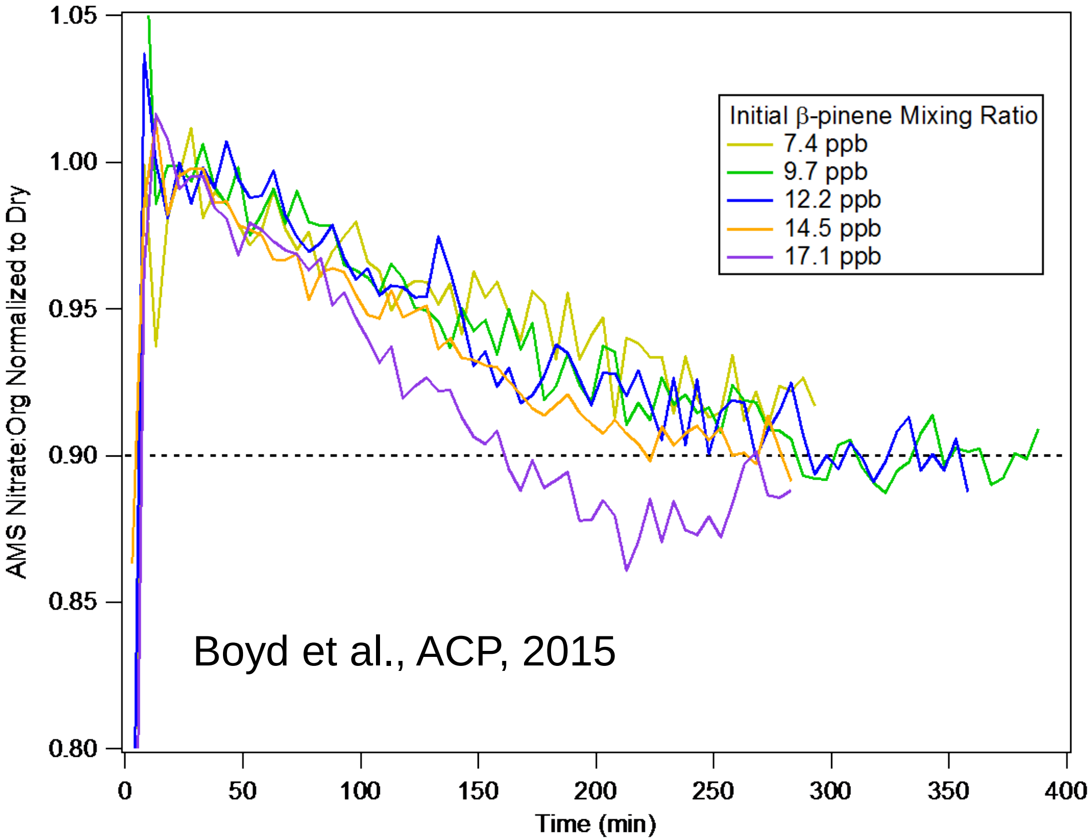
Fate of Atmospheric Organic Nitrates



- **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**

β-pinene+NO_3: Organic Nitrate Hydrolysis

$$\frac{\text{Nitrate/Org in wet expt}}{\text{Nitrate/Org in dry expt}}$$



Boyd et al., ACP, 2015

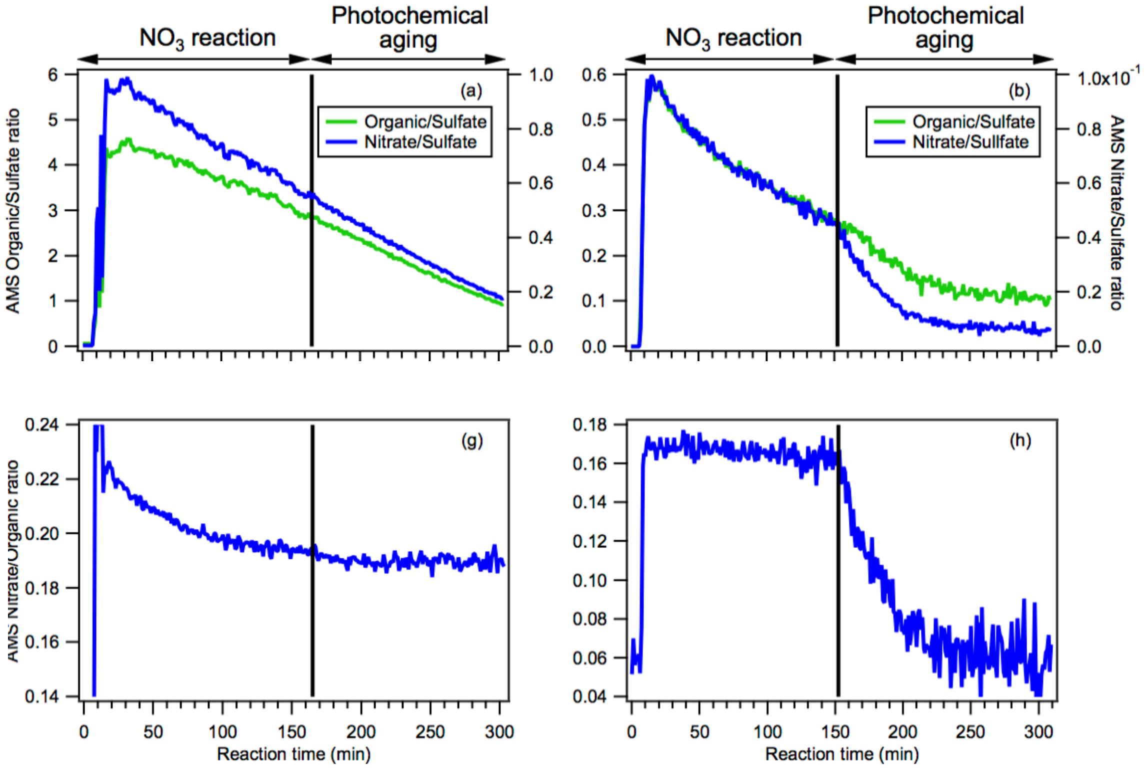
- ~90% of ON is likely primary (which do not hydrolyze at appreciable rates)
- ~10% of ON hydrolyzes with a lifetime of 3-4.5 hr (tertiary ON)

  Much higher than primary/tertiary ON ratio predicted from photooxidation under high NOx conditions (Browne et al., 2013)

- **What happens to ON that do not hydrolyze? (do they get photolyzed /OH reaction?)**

Photochemical Aging of Nighttime Aerosol

β-pinene + NO_3 α-pinene + NO_3



- Photochemically aging, OH + hυ
- 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.

Photochemical Fate of Organic Nitrates:
→ VOC/composition dependent!

Nah et al., ES&T, 2016

Conclusions

- Submicron non-refractory PM1 in SE US dominated by organics.

- Isoprene-OA accounts for 18-36% of total OA in summer
  - Isoprene-OA formation is greatly and directly regulated by SO4
  - 1 μg m^{-3} reduction in sulfate is associated with 0.23-0.42 μg m^{-3} reduction in Isoprene-OA.

- LO-OOA accounts for 22-34% of total OA
  - Likely originates from monoterpenes, and its formation could be controlled by nighttime NO_3 chemistry (NO_x effect).
  - Organic nitrates makes up a substantial fraction (up to 12% in summer) of ambient OA in SE US

- Chamber studies provide fundamental data to interpret ambient observation
  - 60-80% of OA are organic nitrates
  - Formation of highly oxygenated ON species in both gas- and particle-phase, many of which observed in the ambient
  - Photochemical fate and hydrolysis of organic nitrates depends on parent compound and oxidation

Synergistic chamber and ambient studies → more insights!

Question: Mechanism and Magnitude of Anthropogenic Influence on Biogenic SOA Formation?

NO_x and SO_4 together can potentially control 43-70% of OA (30-50% of PM_1) in the SE US during summer.

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