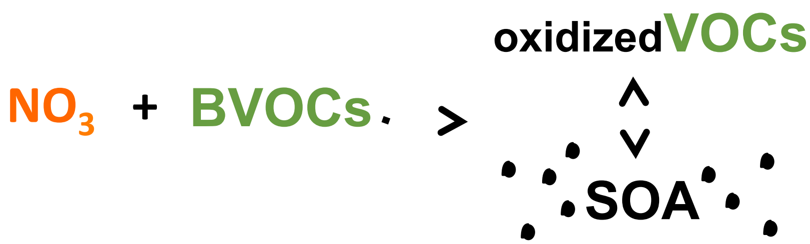
NO_3-initiated biogenic SOA production: Insights from field and chamber studies



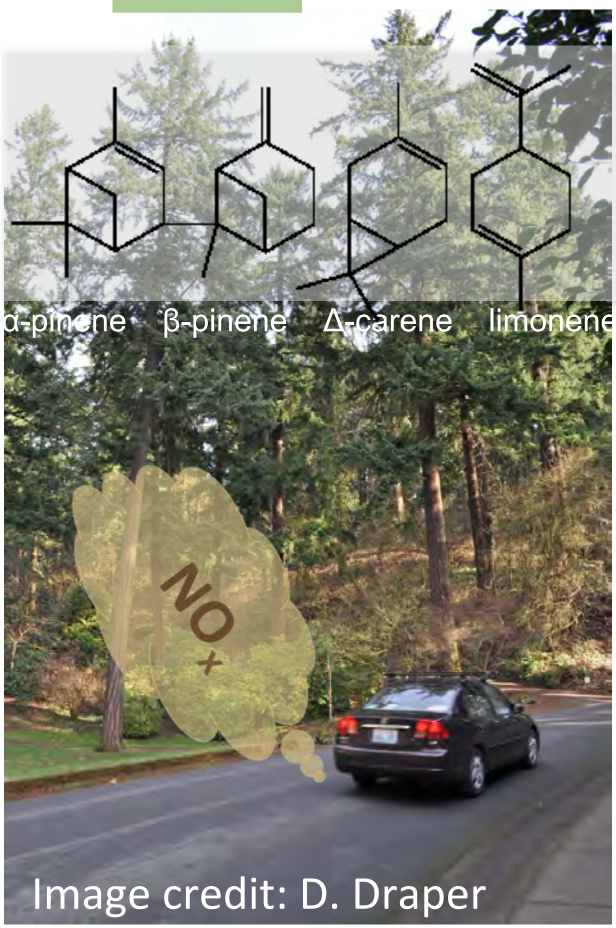
Julie Fry, Ben Ayres, Danielle Draper, Hannah Allen, Kang Kang
Reed College
With many of our favorite partners: Steve Brown (NOAA CSD), Jose Jimenez, Doug Day, Sam Thompson, Weiwei Hu, Pedro Campuzano-Jost (CU Boulder), Delphine Farmer, Yury Desyaterik (CSU)

249th ACS National Meeting
Atmospheric Chemistry session
Mar. 24, 2015

Background: NO_3 and monoterpenes (C_{10} BVOCs)

O_3 / NO_3 / OH + BVOCs → oxidized VOCs ↔ SOA

BVOCs:



$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
$$NO_3 + h\nu \rightarrow NO_2 + O$$

*NO_3 is rapidly photolyzed and thus present primarily at night, in equil with N_2O_5:

$$NO_3 + NO_2 \leftrightarrow N_2O_5$$

Typical concentrations:
12 h nighttime avg [NO_3]: 5×10^{8} #/cm^3
24 h avg [O_3]: 7×10^{11} #/cm^3
(Atkinson & Arey, 2003)

BVOC lifetimes w.r.t. each oxidant

BVOC	O_3	NO_3
α-pinene	4.7 hr	5.4 min
β-pinene	1.1 day	13 min
Δ-carene	11 hr	3.7 min
limonene	1.9 hr	2.7 min

What's to come in this talk

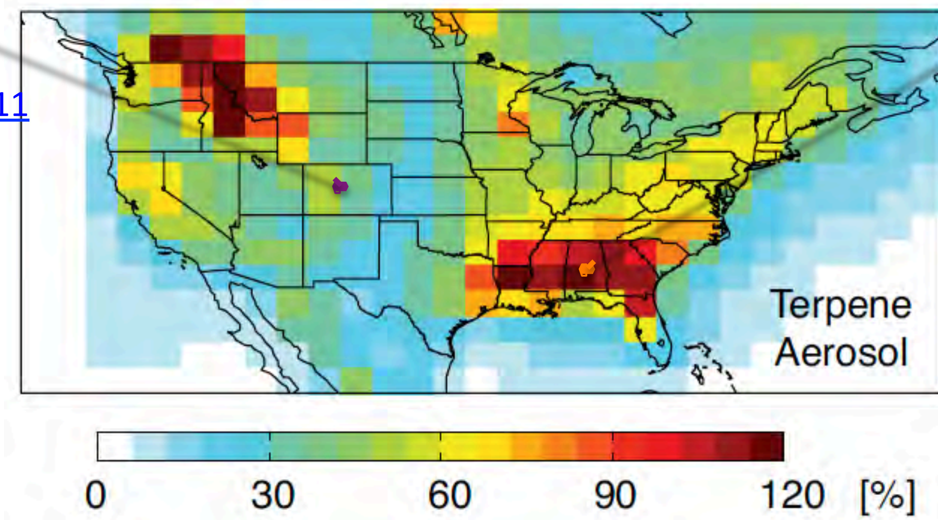
- **Field evidence** of the importance of NO_3 + BVOC chemistry for organic aerosol formation (BEACHON-RoMBAS 2011, SOAS 2013)
- NCAR **chamber studies** showing high & variable SOA yields from NO_3 oxidation of various BVOC, with the **notable exception of α-pinene**
- Reed **chamber studies** exploring O_3 vs. NO_3 + BVOCs find **compositional reasons** for α-pinene's exceptionalism
- CU Boulder **chamber studies**: Does **RO_2 radical fate** matter?

BEACHON 2011 vs. SOAS 2013 campaigns: Observing NO_3 + terpenes in 2 forests

BEACHON Rocky Mountain Biogenic Aerosol Study, July-Aug. 2011

http://tinyurl.com/BEACHON2011

Montane ponderosa pine;
8000 ft elevation



Background map from Pye et al., ACP 2010: % enhancement of terpenes OA due to addition of NO_3 pathway

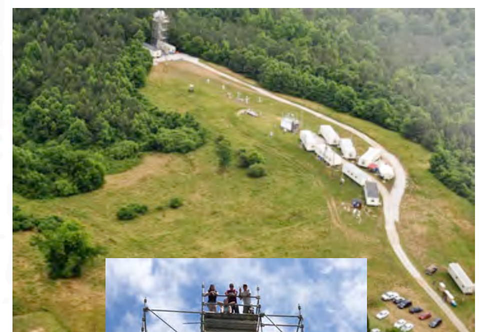
NO_3 + terpenes contribute 4 Tg/yr SOA globally (20% of total BSOA production), with large regional variability

(Uses NO_3 + β-pinene SOA yield parameterization for *all* NO_3+terpene reactions)

SOAS: Southern Oxidant and Aerosol Study, Jun-July 2013

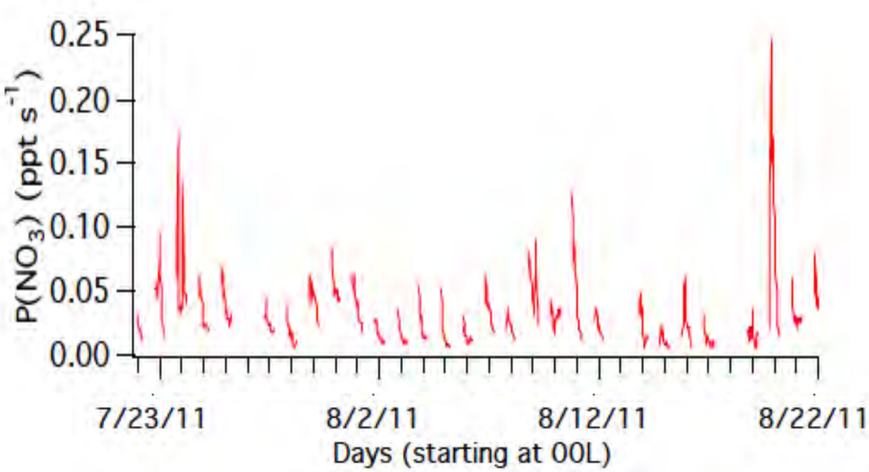
http://soas2013.rutgers.edu/

Humid subtropical forest;
240 ft elevation

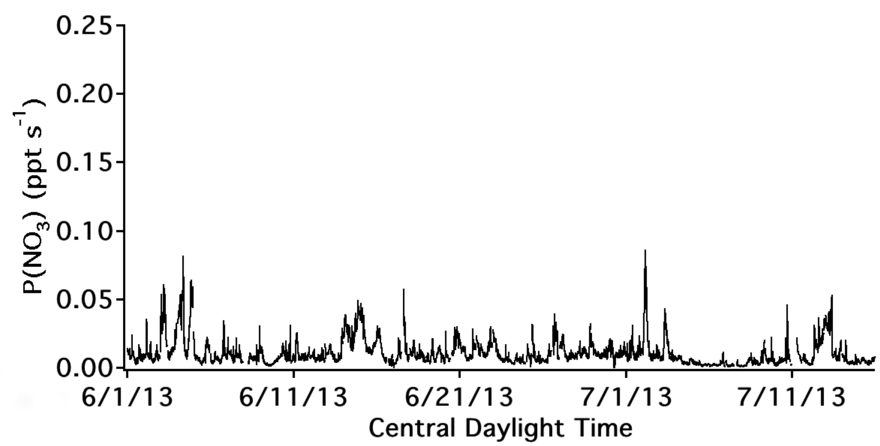


BEACHON 2011 vs. SOAS 2013 campaigns: Observing NO_3 + terpenes in 2 forests
1. The oxidant: NO_3

BEACHON Rocky Mountain Biogenic Aerosol Study, July-Aug. 2011



SOAS: Southern Oxidant and Aerosol Study, Jun-July 2013



$$P(NO_3) = 1.4 \times 10^{-13} e^{-2470/T} [NO_2][O_3]$$

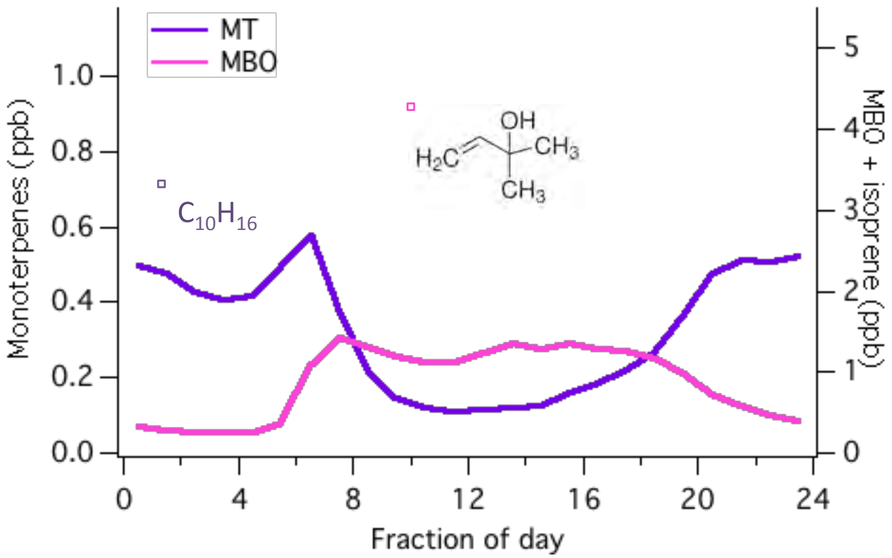
⇒ Both relatively low-NOx, remote regions (peaks < 4 ppb NO_2),

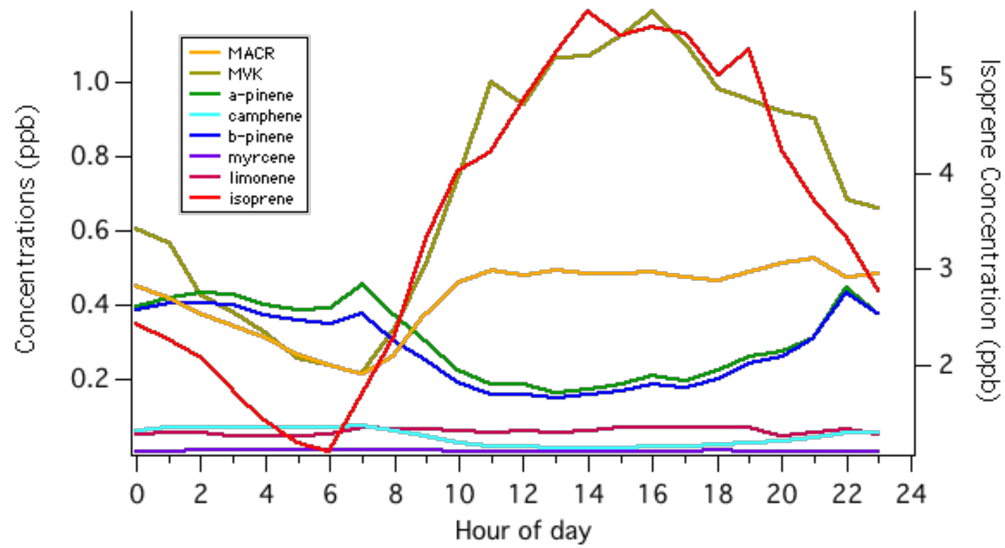
⇒ Nightly NO_3 production nevertheless substantial (up to 3 ppb / night)

BEACHON 2011 vs. SOAS 2013 campaigns: Observing NO_3 + terpenes in 2 forests 2. The terpenes

BEACHON Rocky Mountain Biogenic Aerosol Study, July-Aug. 2011

SOAS: Southern Oxidant and Aerosol Study, Jun-July 2013



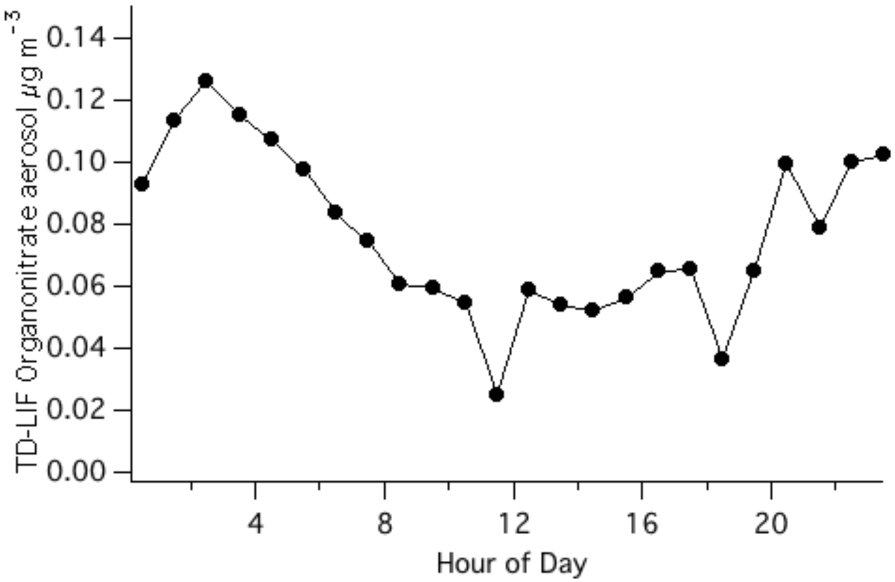


Monoterpenes ($C_{10}H_{16}$) @ BEACHON:
~ 1:1:1 α-pinene, β-pinene, Δ-carene

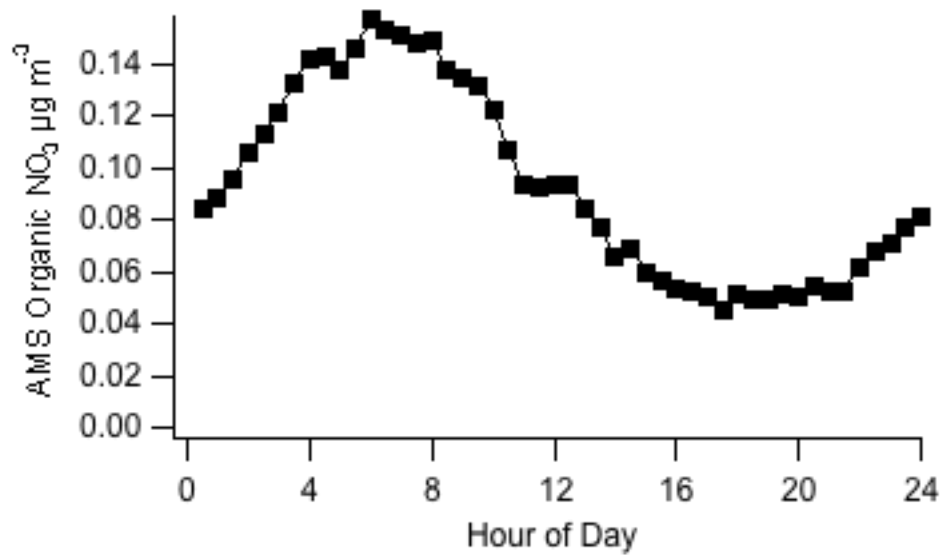
VOC data courtesy L. Kaser/A. Hansel; A. Koss/J. de Gouw/A. Goldstein

BEACHON 2011 vs. SOAS 2013 campaigns: Observing NO_3 + terpenes in 2 forests
3. Organonitrate aerosol

BEACHON Rocky Mountain Biogenic Aerosol Study, July-Aug. 2011



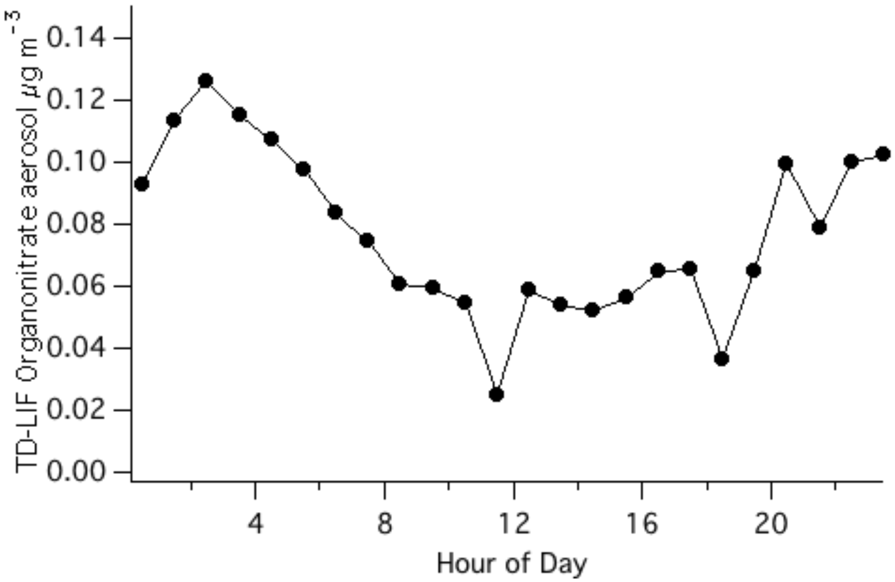
SOAS: Southern Oxidant and Aerosol Study, Jun-July 2013



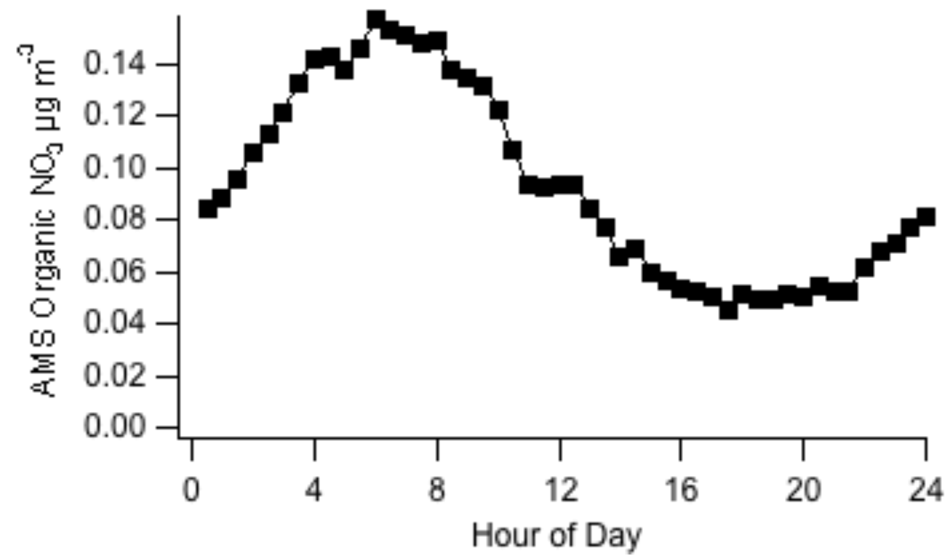
Organonitrate measurements courtesy Ron Cohen (UC Berkeley); AMS Jose Jimenez (CU)

BEACHON 2011 vs. SOAS 2013 campaigns: Observing NO_3 + terpenes in 2 forests 3. Organonitrate aerosol

BEACHON Rocky Mountain Biogenic Aerosol Study, July-Aug. 2011



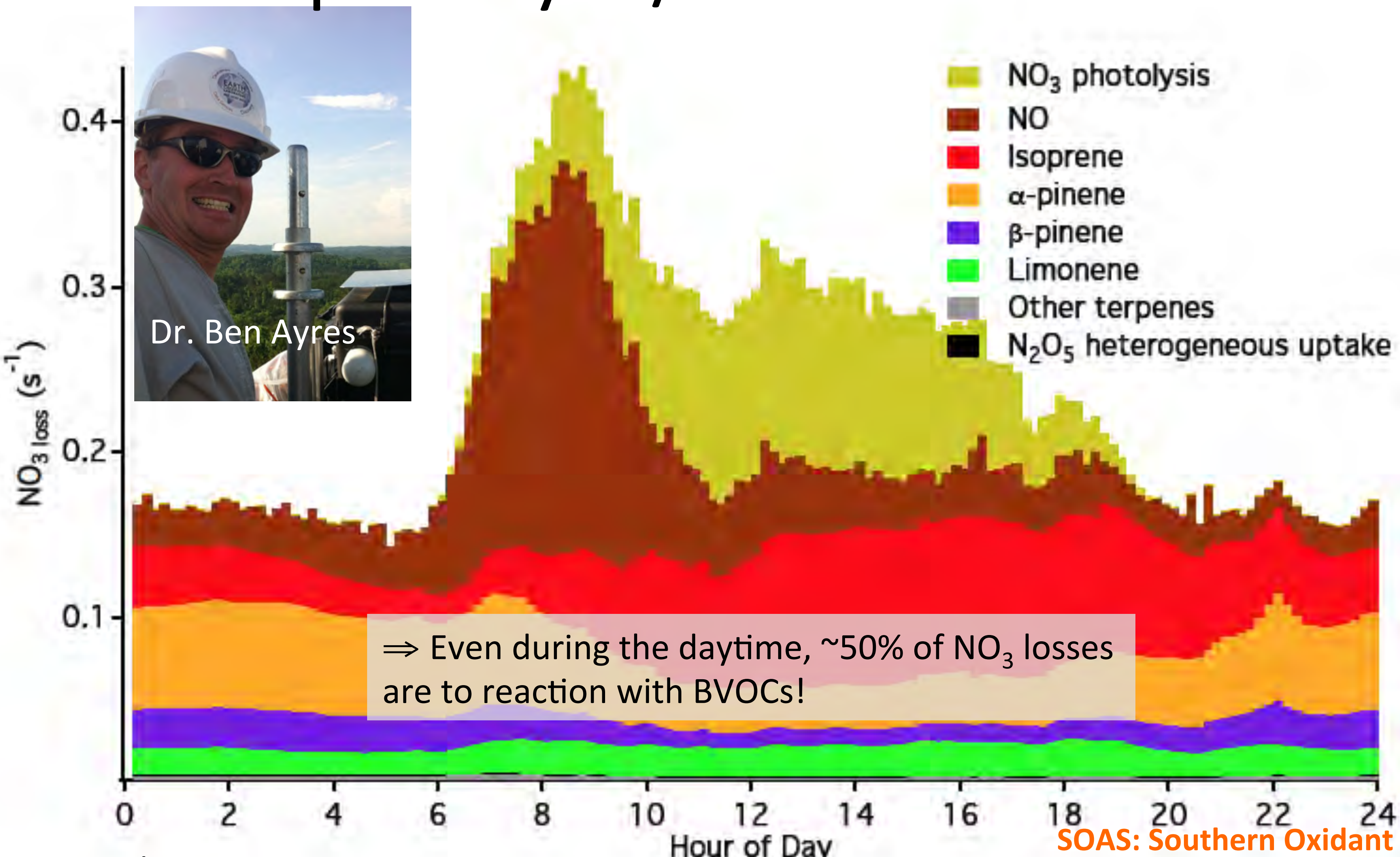
SOAS: Southern Oxidant and Aerosol Study, Jun-July 2013



Two very different forests ....

Two very similar organonitrate aerosol diurnal cycles!

NO_3 losses: Reaction with BVOC vs. photolysis/NO reactions

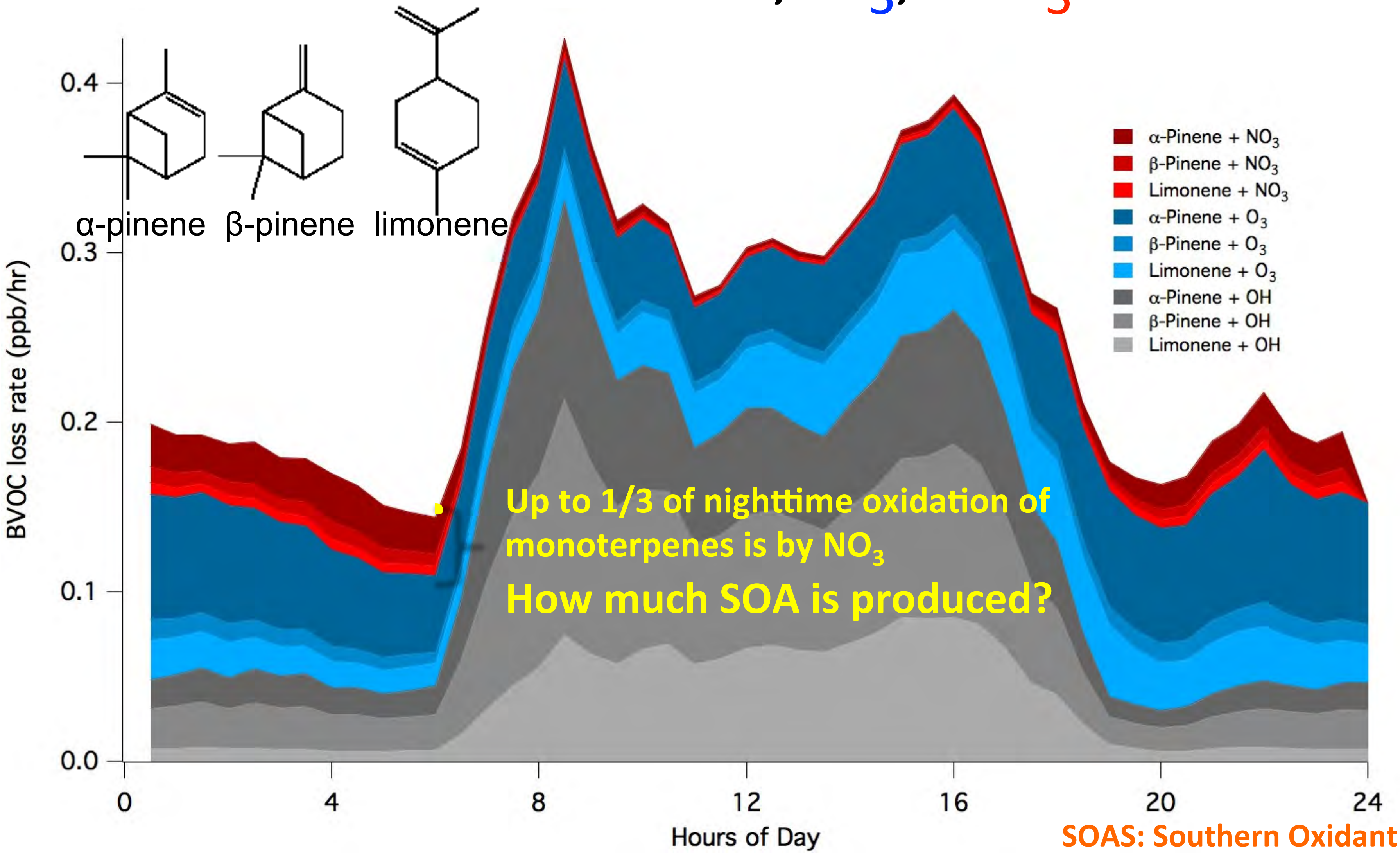


⇒ Even during the daytime, ~50% of NO_3 losses are to reaction with BVOCs!

Ayres et al., 2015, in prep

SOAS: Southern Oxidant and Aerosol Study, Jun-July 2013

Rate of monoterpene losses to each oxidant: OH, O_3, NO_3



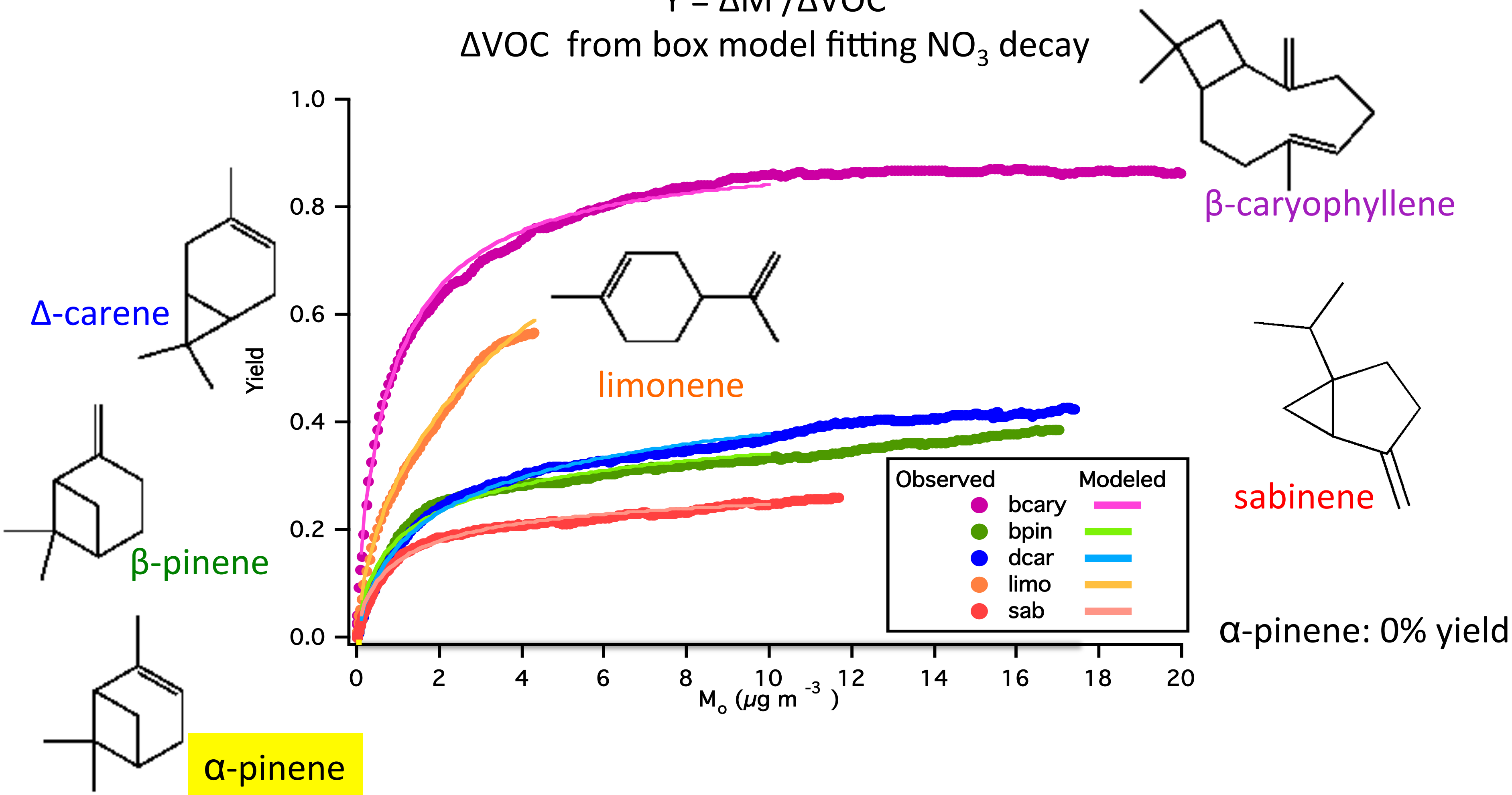
Rate = k_{ox+VOC} [ox][VOC]

SOAS: Southern Oxidant and Aerosol Study, Jun-July 2013

What does NO_3 oxidation mean for SOA formation? NCAR chamber 2011: It depends! Which terpene?

$Y = \Delta M / \Delta VOC$

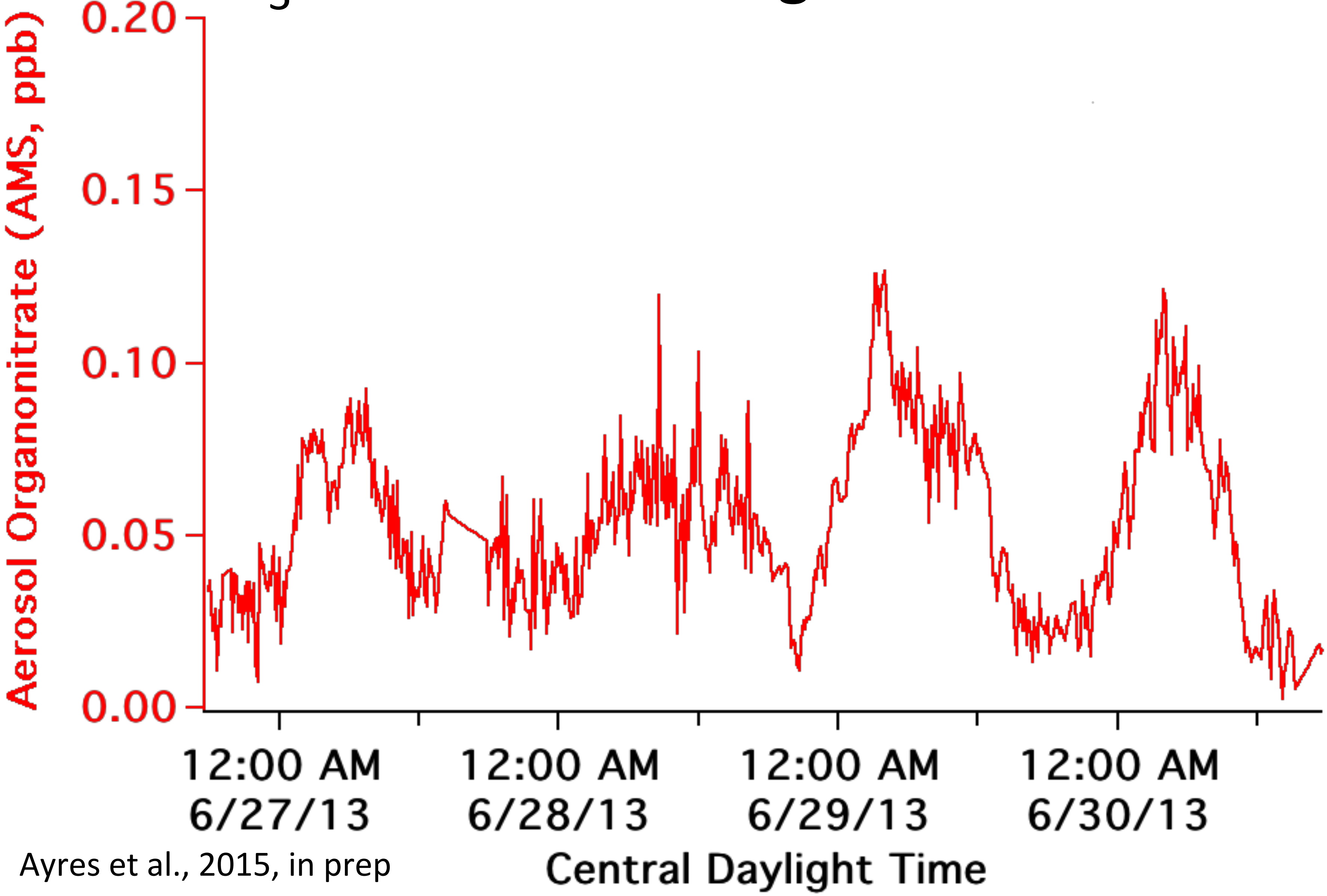
ΔVOC from box model fitting NO_3 decay



Low concentration (~ 10 ppb each) experiments only

Fry et al., ES&T 2014

Back to SOAS data: Demonstrating that NO_3+BVOC makes organonitrate SOA



Ayres et al., 2015, in prep

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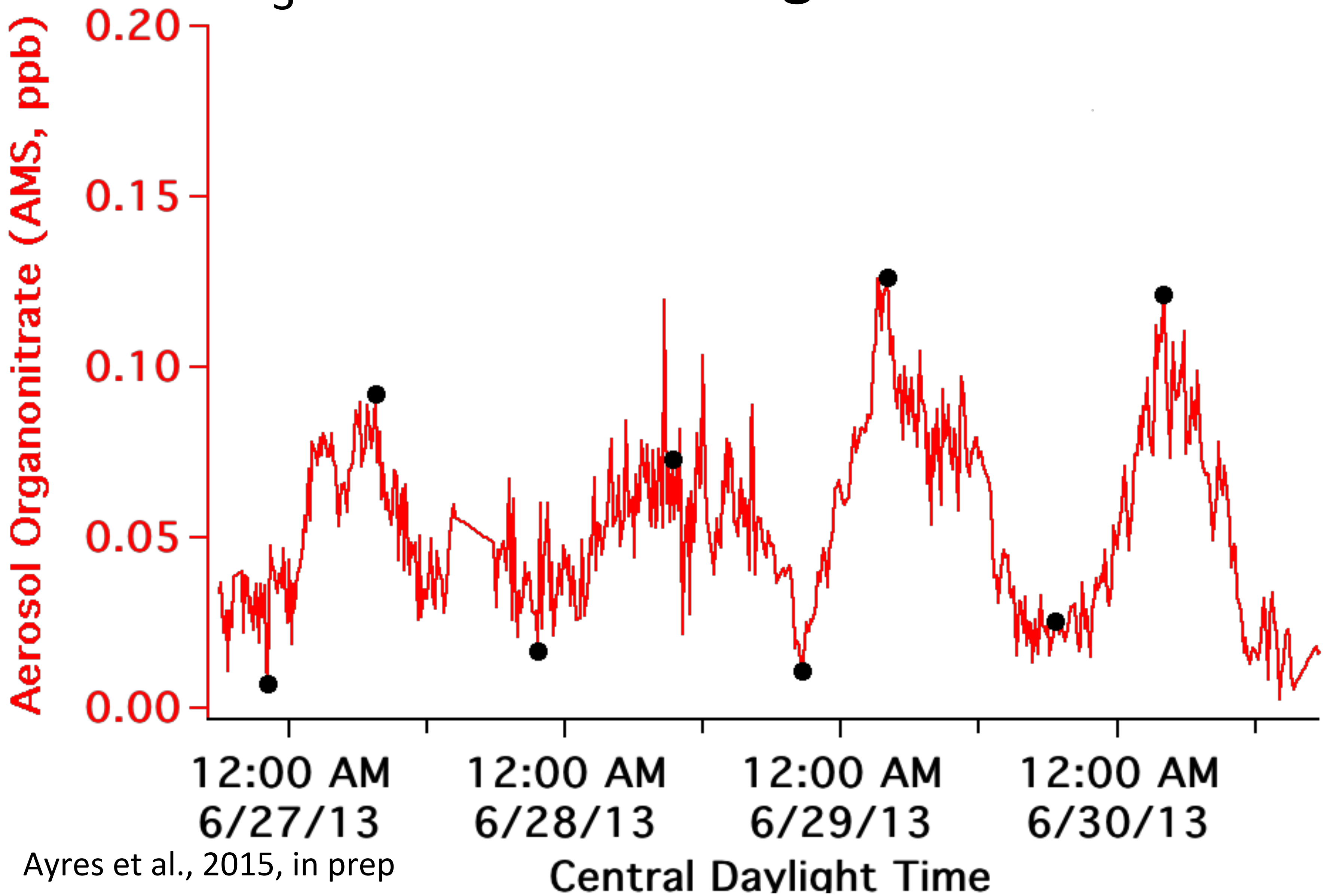

Ayres et al., 2015, in prep

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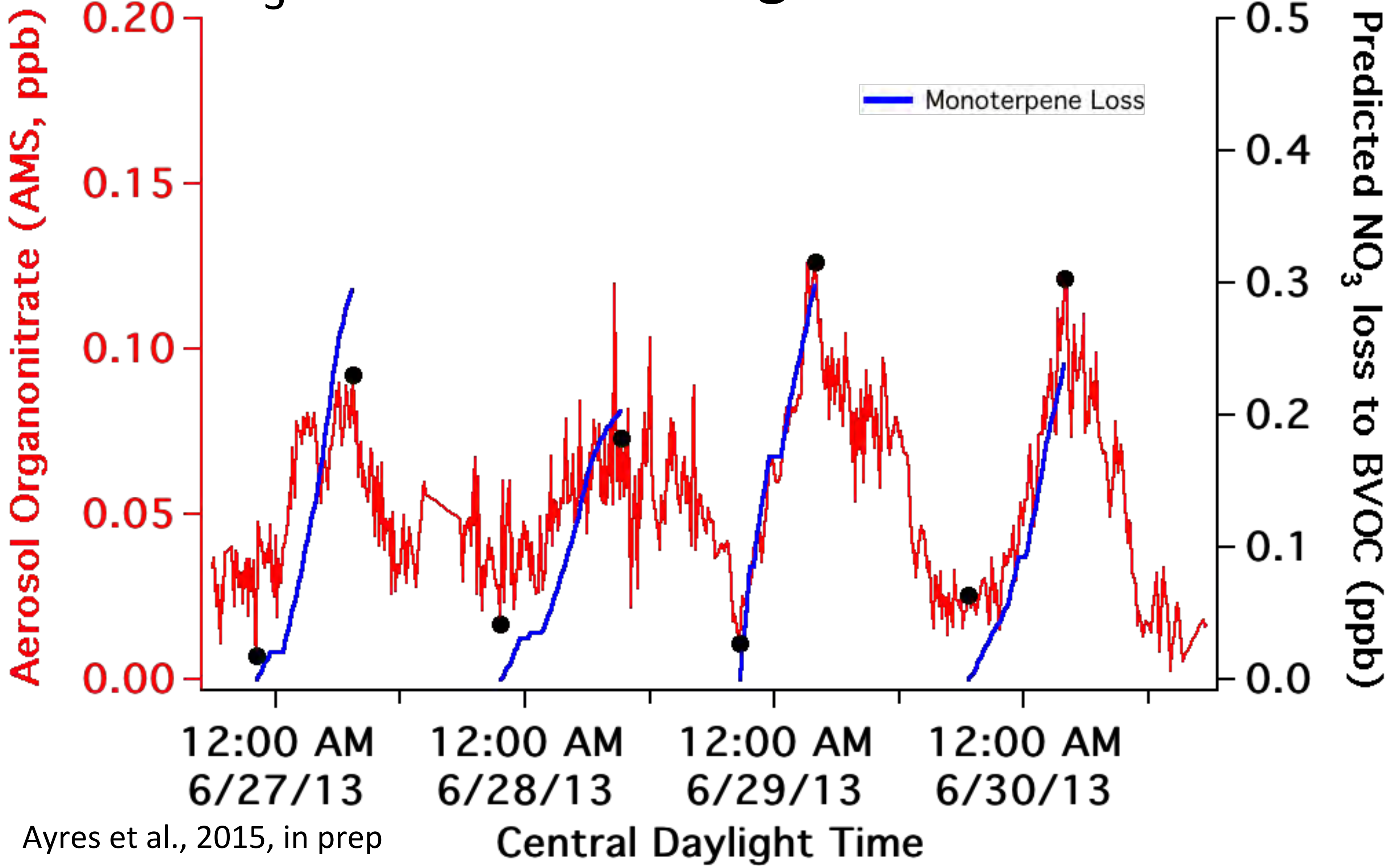
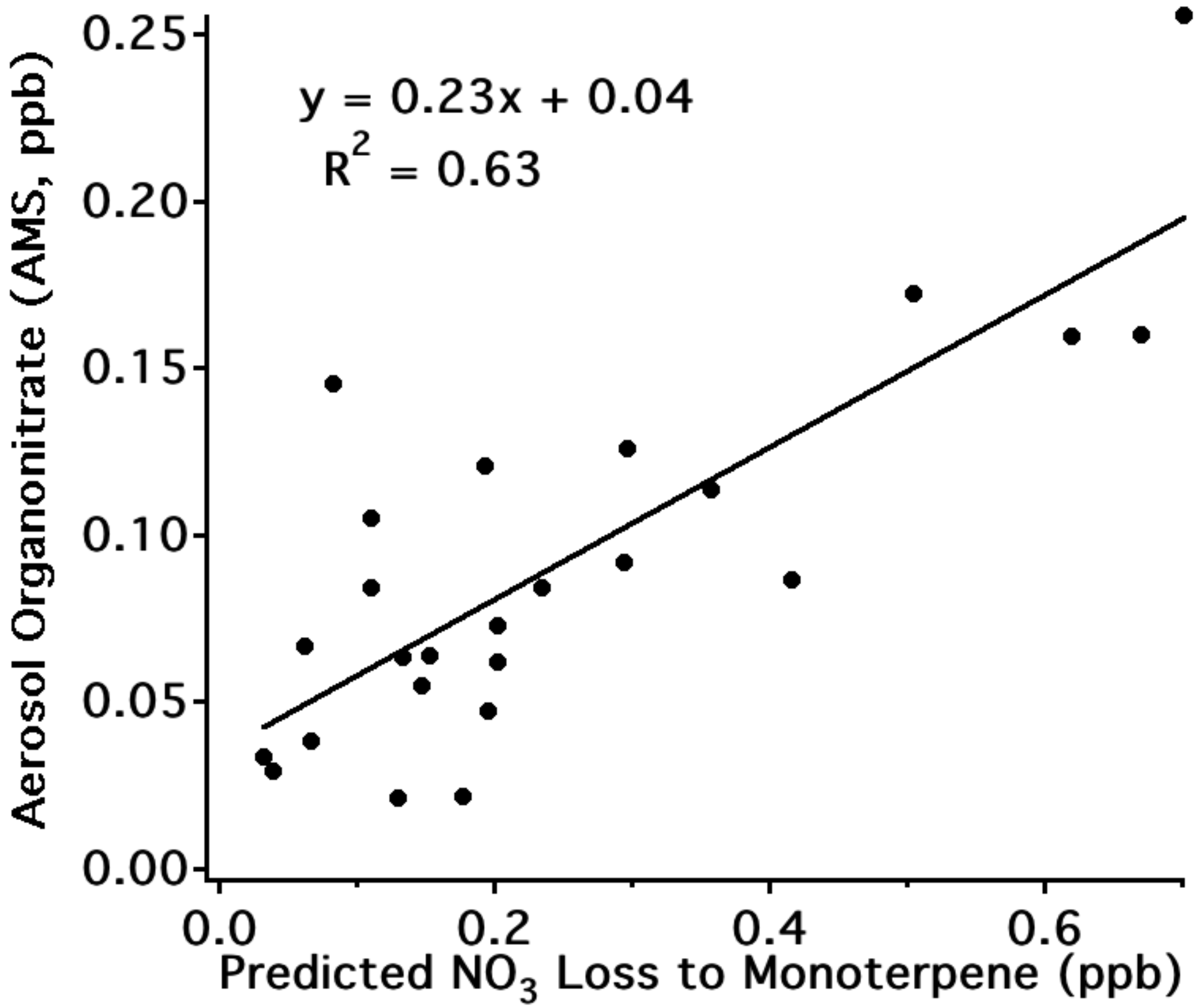


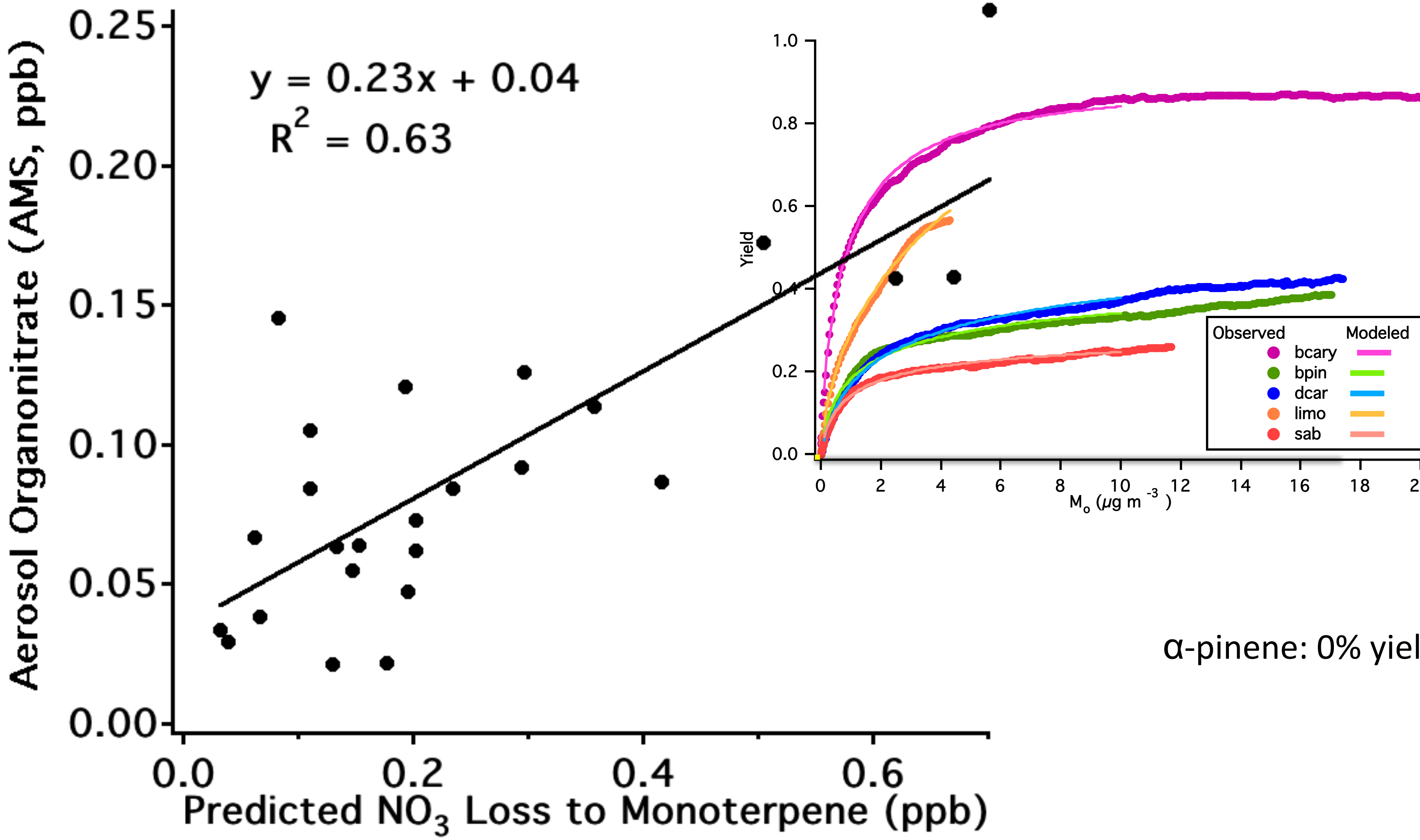
Ayres et al., 2015, in prep

Aggregate molar organonitrate$_{aero}$ yield ~ 23 %



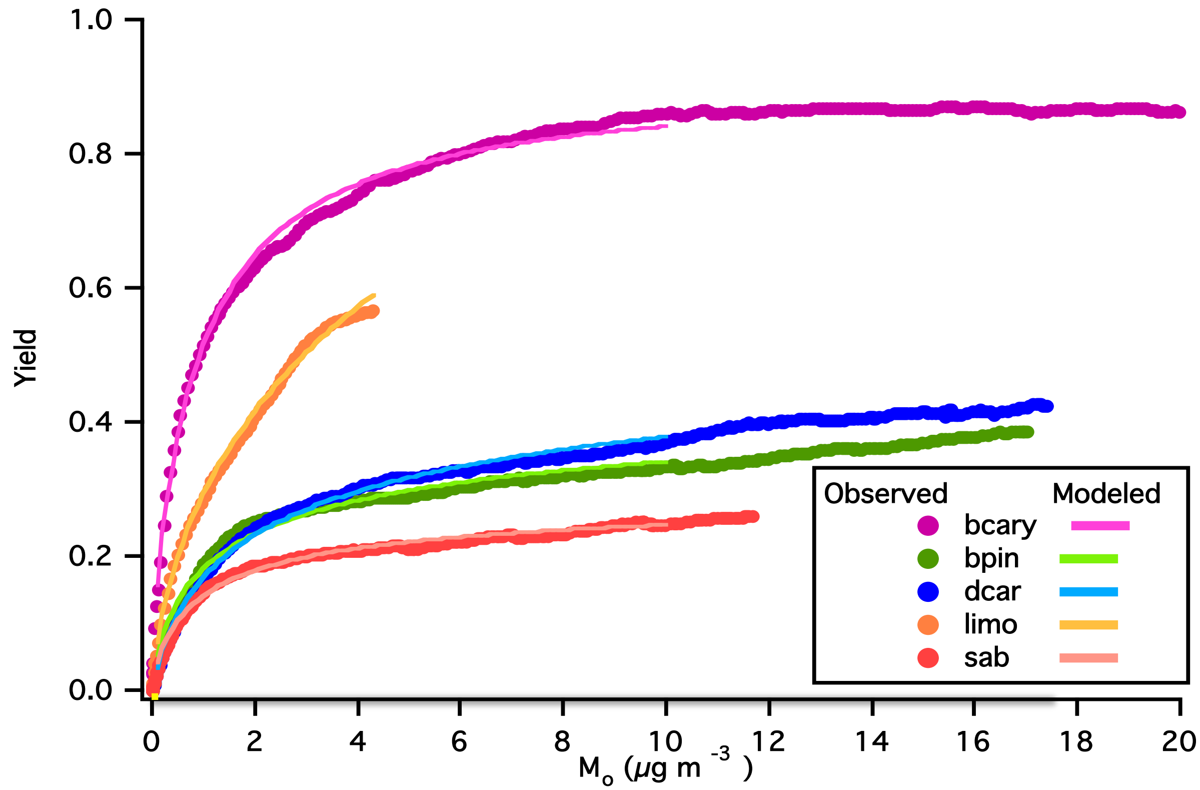
Ayres et al., 2015, in prep

Aggregate molar organonitrate$_{aero}$ yield ~ 23 %
Recall: α-pinene yield = 0! Higher SOA yields from other BVOCs compensate



α-pinene: 0% yield!

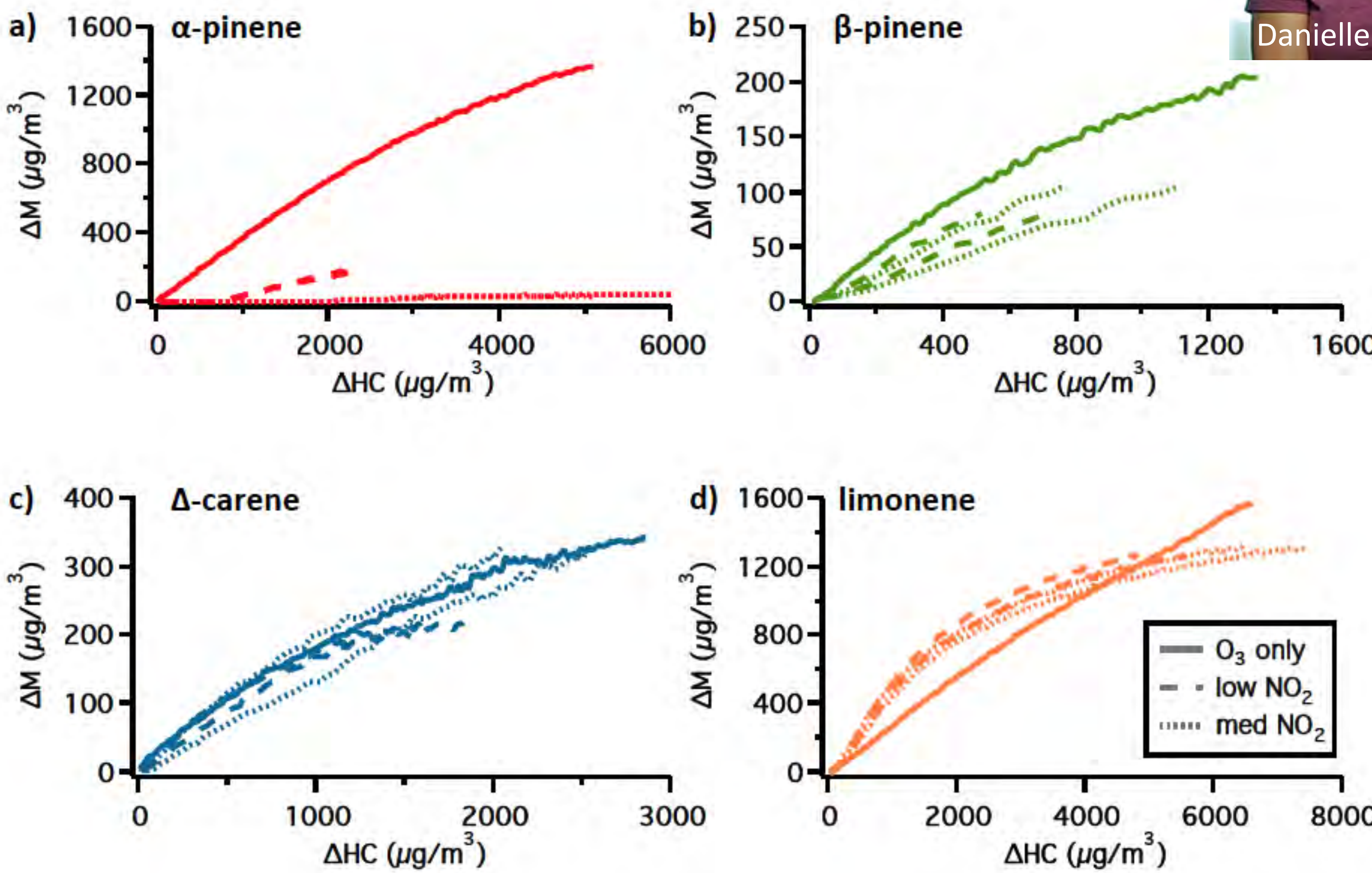
Aggregate molar organonitrate yield ~ 23 %
Recall: α-pinene yield = 0! Higher SOA yields from other BVOCs compensate



N_2O_5 oxidant source
=> Will α-pinene have same "outlier" behavior with O_3 + NO_2?

α-pinene: 0% yield!

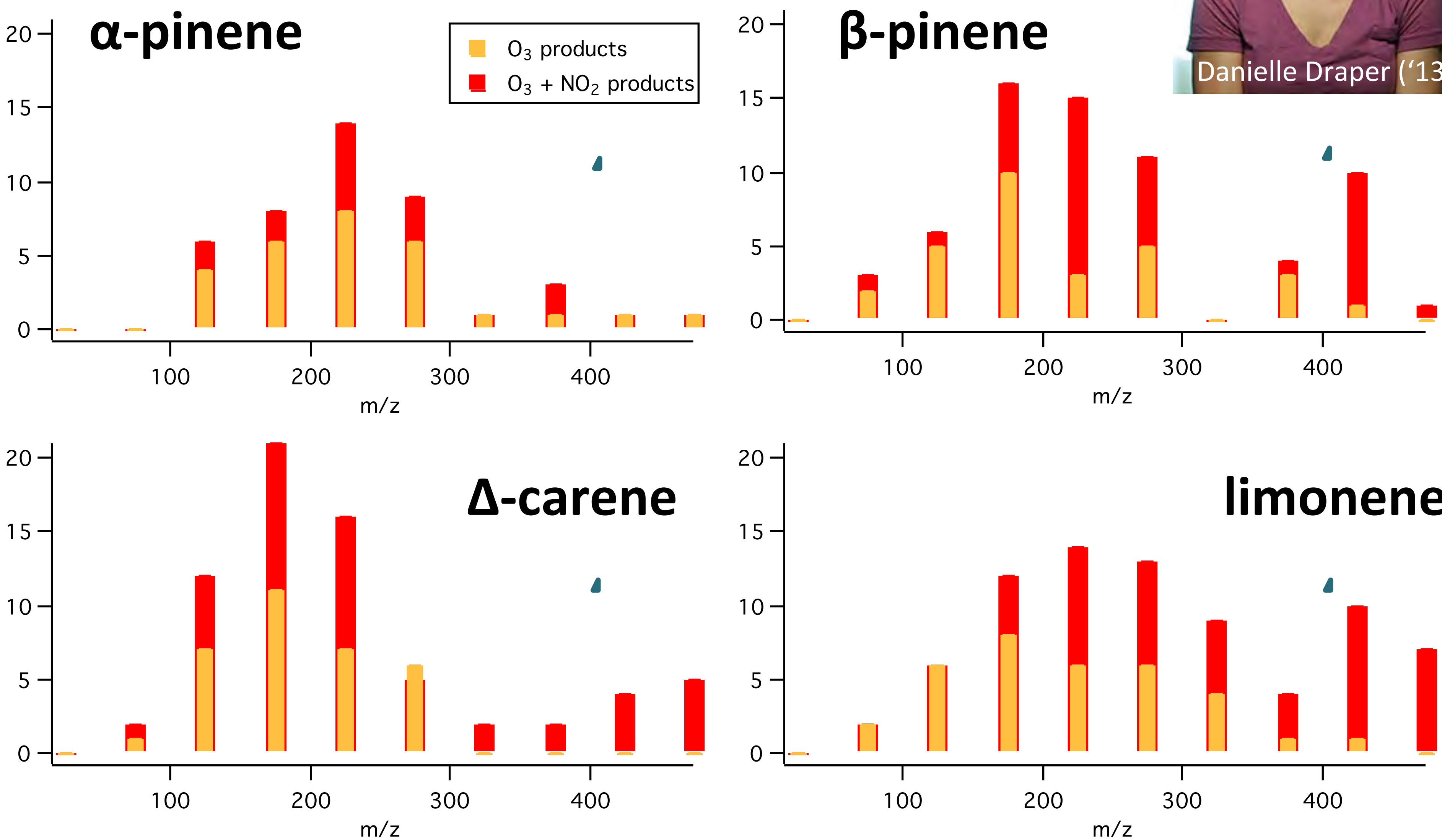
@ Reed Environmental Chamber 2012-2013: Comparing mass yields for O_3 + BVOC at varying $[NO_2]$



Draper et al., 2015, in prep

MW comparison from HPLC-ESI-MS

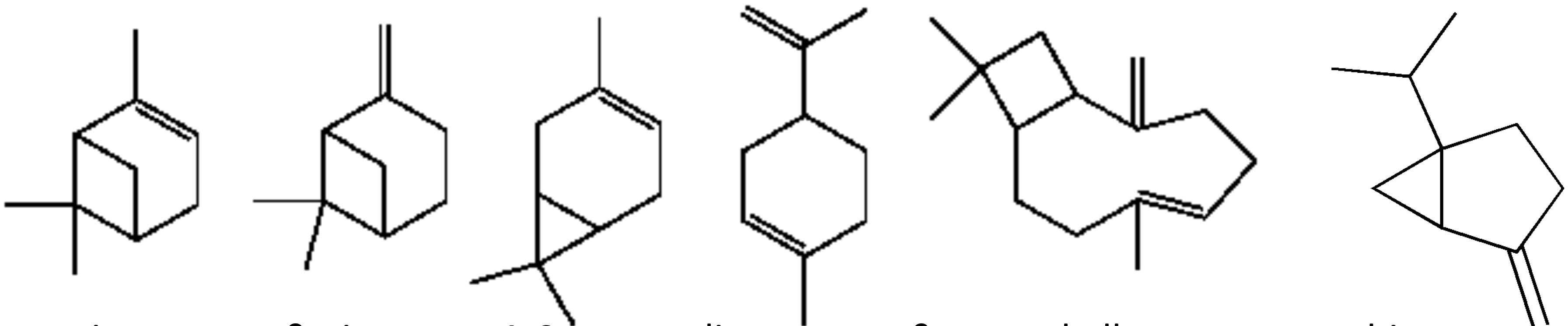
Histograms showing distributions of product masses for each monoterpene with just O_3 vs. with $O_3 + NO_2$:



Draper et al., 2015, in prep; collaboration with **Delphine Farmer** and **Yury Desyaterik** (CSU)

Conclusions & questions remaining after the NCAR & Reed NO_3 + terpene chamber experiments

- Highly variable SOA yields observed for various terpenes:

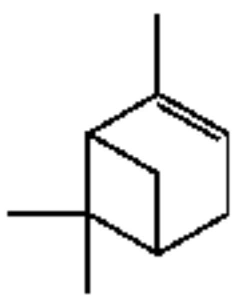


α-pinene	β-pinene	Δ-3-carene	limonene	β-caryophyllene	sabinene
0%	40%	40%	60%	80%	30%

- *Higher* MW products observed from NO_3 oxidation than O_3 of all but α-pinene
- **Why does NOx only apparently suppress SOA formation from α-pinene?**

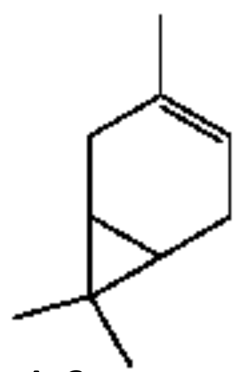
Next round of NO_3 + terpene chamber studies: Is low α-pin yield a function of chamber-specific RO_2 fate? @CU Boulder summer 2014

- Test SOA formation from NO_3 + α-pinene and Δ-carene, at varying relative []'s of VOC, NO_3, and HO_2
- Is the observation of ***large*** SOA yield from NO_3 + Δ-carene and ***no*** SOA yield from NO_3 + α-pinene robust across varying RO_2 radical fate?



α-pinene

0%

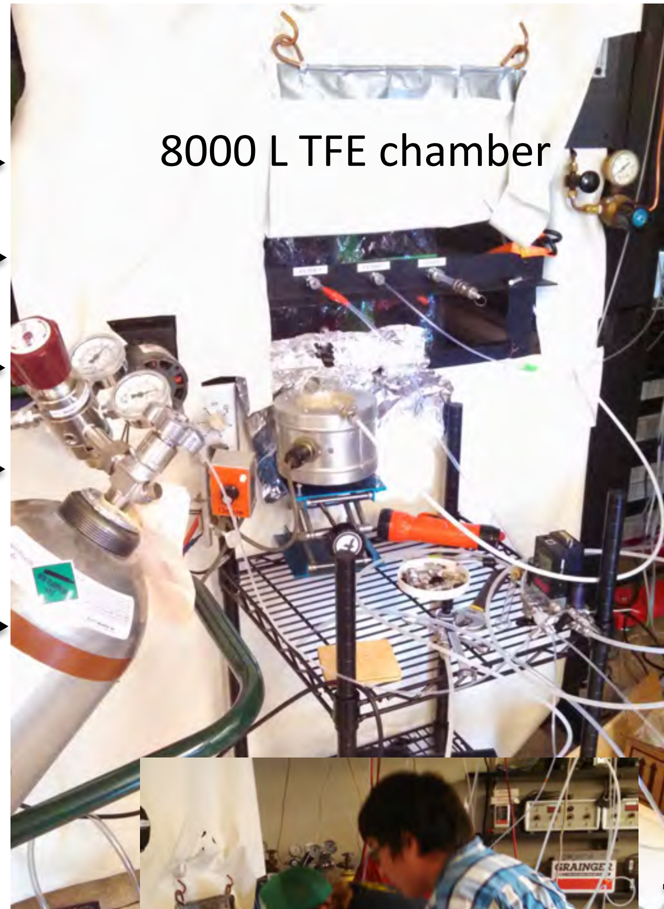


Δ-3-carene

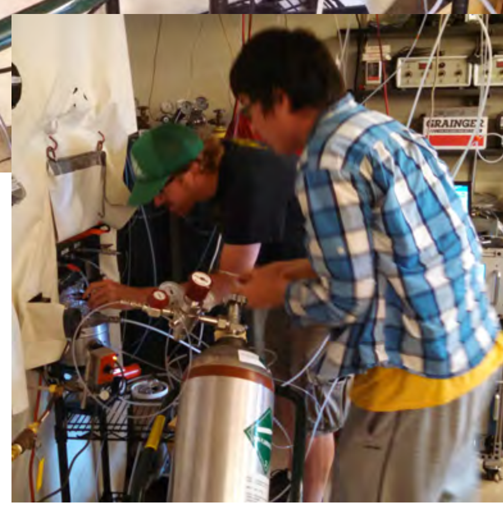
40%

NO_3 + terpenes @CU Boulder 8000 L chamber, 2014

- Zero air →
- N_2O_5 trap →
- BVOC bulb →
- HCHO bulb →
- Seed aerosol atomizer $(NH_4)_2SO_4$ →



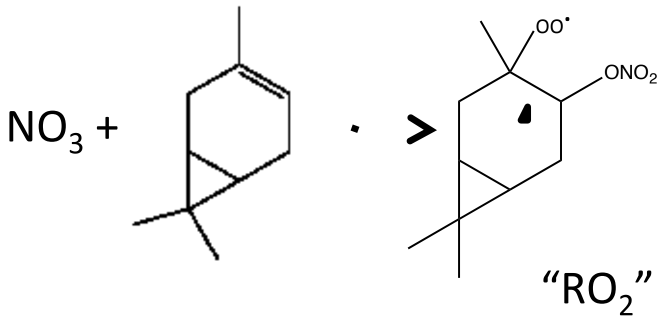
- → N_2O_5 /NO_3 CRDS trap
- → AMS
- → SMPS
- → UCPC
- → I- CIMS
- → NO_x box
- → O_3 monitor
- → CO_2 & H_2O (LiCor)



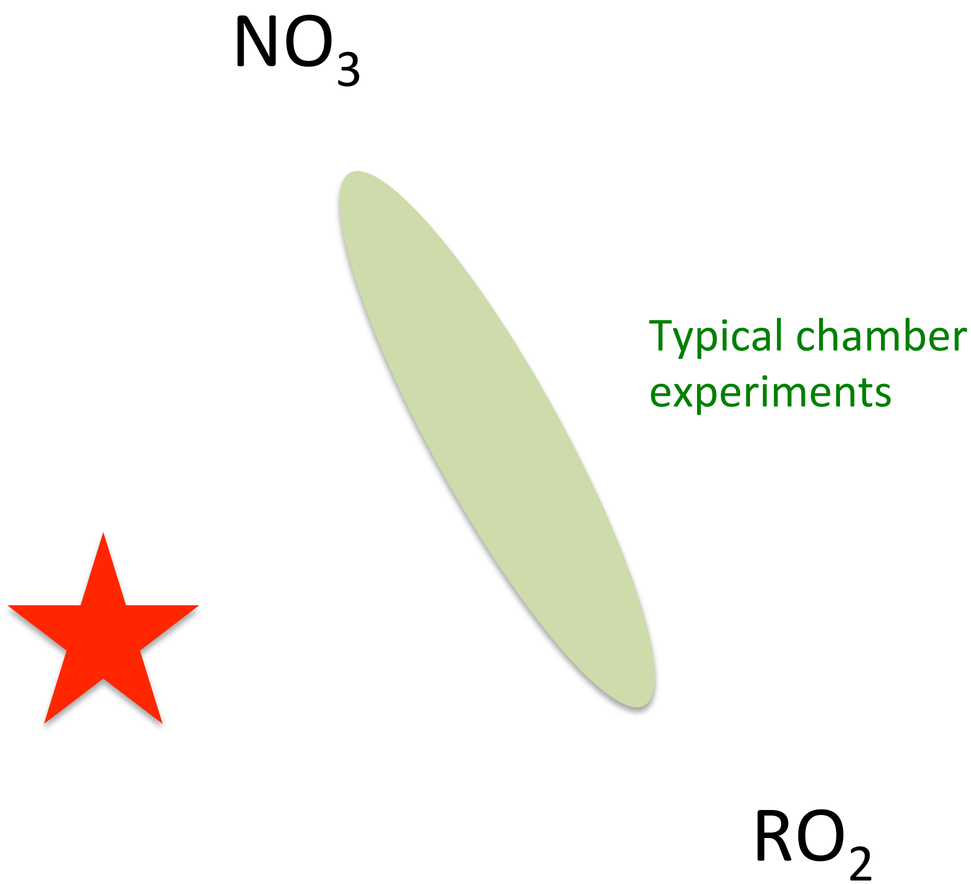
Ben Ayres & Kang Kang, Doug Day, Sam Thompson, Harald Stark, Pedro Campuzano-Jost, Weiwei Hu, Jose Jimenez, Steve Brown

Thanks to April Ranney, Demetrios Pagonis, and Paul Ziemann for chamber & GC help!

Obtaining conditions of varying, controlled RO_2 fate:



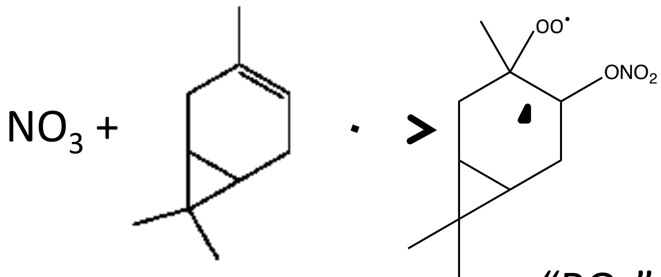
What is most likely reaction partner for RO_2?



Obtaining conditions of varying, controlled RO_2 fate:

100 ppb N_2O_5, 10 ppb VOC

NO_3



"RO_2"

What is most likely reaction partner for RO_2?

HO_2

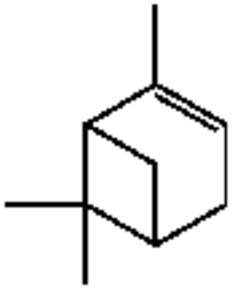
Add HCHO to chamber before VOC (nominally 50 ppm)

Continuous N_2O_5 injection, 10 ppb VOC

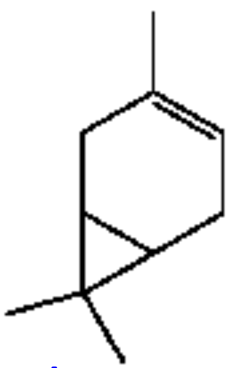
RO_2

10 ppb N_2O_5, 100 ppb VOC

α-pinene and Δ-carene yields not affected by RO_2 fate, inorganic seed



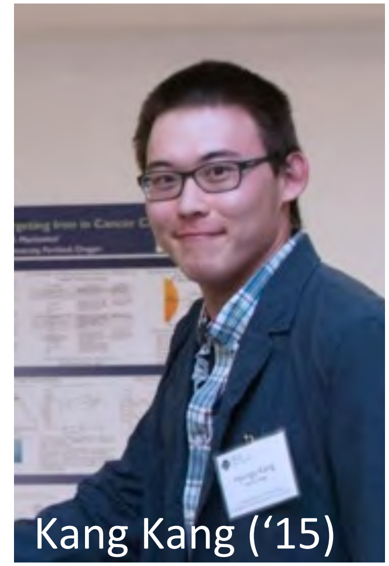
α-pinene



Δ-carene

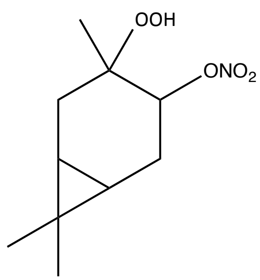
No.	Regime	SOA yield (AMS)	NO_3:Org
6	NO_3+RO_2	**2%**	0.08
14	RO_2+RO_2, seeded	**1%**	0.10
17	HO_2+RO_2	**2%**	0.17
11c	RO_2+RO_2	**25%**	0.09
13	NO_3+RO_2	**37%**	0.15
16	HO_2+RO_2, seeded	**38%**	0.12
18c	RO_2+RO_2, seeded	**38%**	0.06
19	HO_2+RO_2, seeded	**29%**	0.14
22c	RO_2+RO_2	**103%**	0.07
23	HO_2+RO_2	**24%**	0.15

Always ~ 0.1!



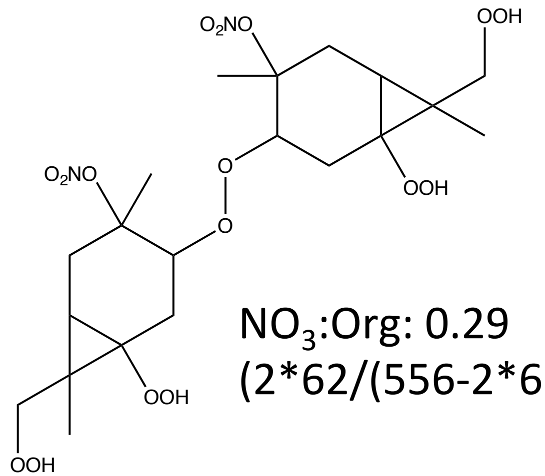
*a caution: our purchased 90% 3-carene from Aldrich contains a substantial contaminant of a C_{10} ketone!

What structures are consistent with the observed NO_3:Org ratio of 0.10 ± 0.05?



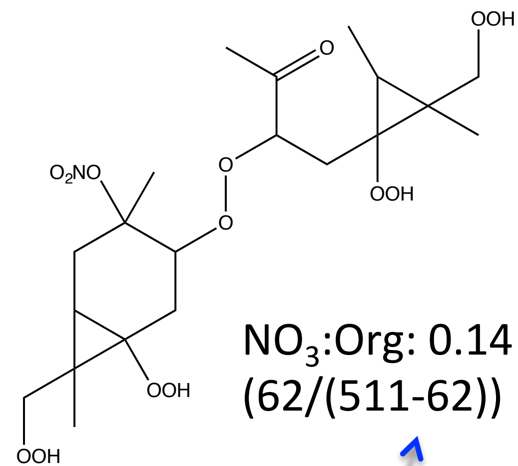
Chemical Formula: $C_{10}H_{17}NO_4$
Molecular Weight: 231.25

NO_3:Org: 0.37
(62/(231-62))



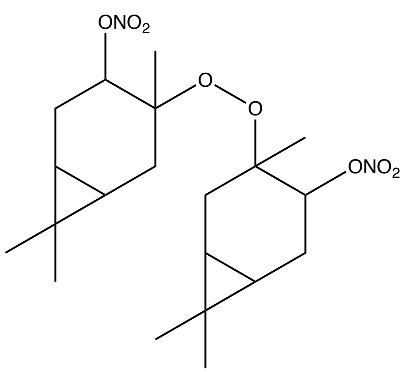
NO_3:Org: 0.29
(2*62/(556-2*62))

Chemical Formula: $C_{20}H_{32}N_2O_{16}$
Molecular Weight: 556.47



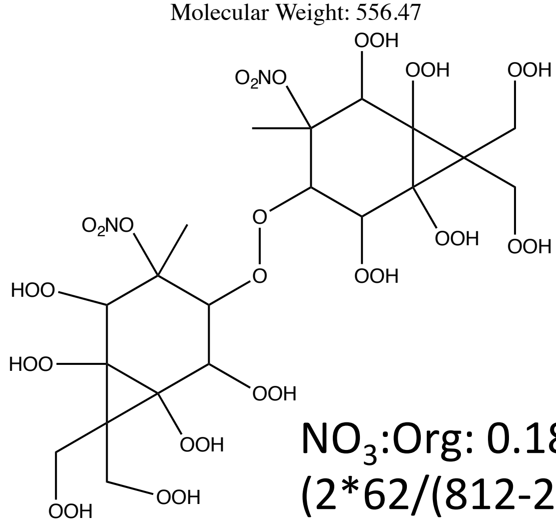
NO_3:Org: 0.14
(62/(511-62))

Chemical Formula: $C_{20}H_{33}NO_{14}$
Molecular Weight: 511.48



Chemical Formula: $C_{20}H_{32}N_2O_8$
Molecular Weight: 428.48

NO_3:Org: 0.41
(2*62/(428-2*62))

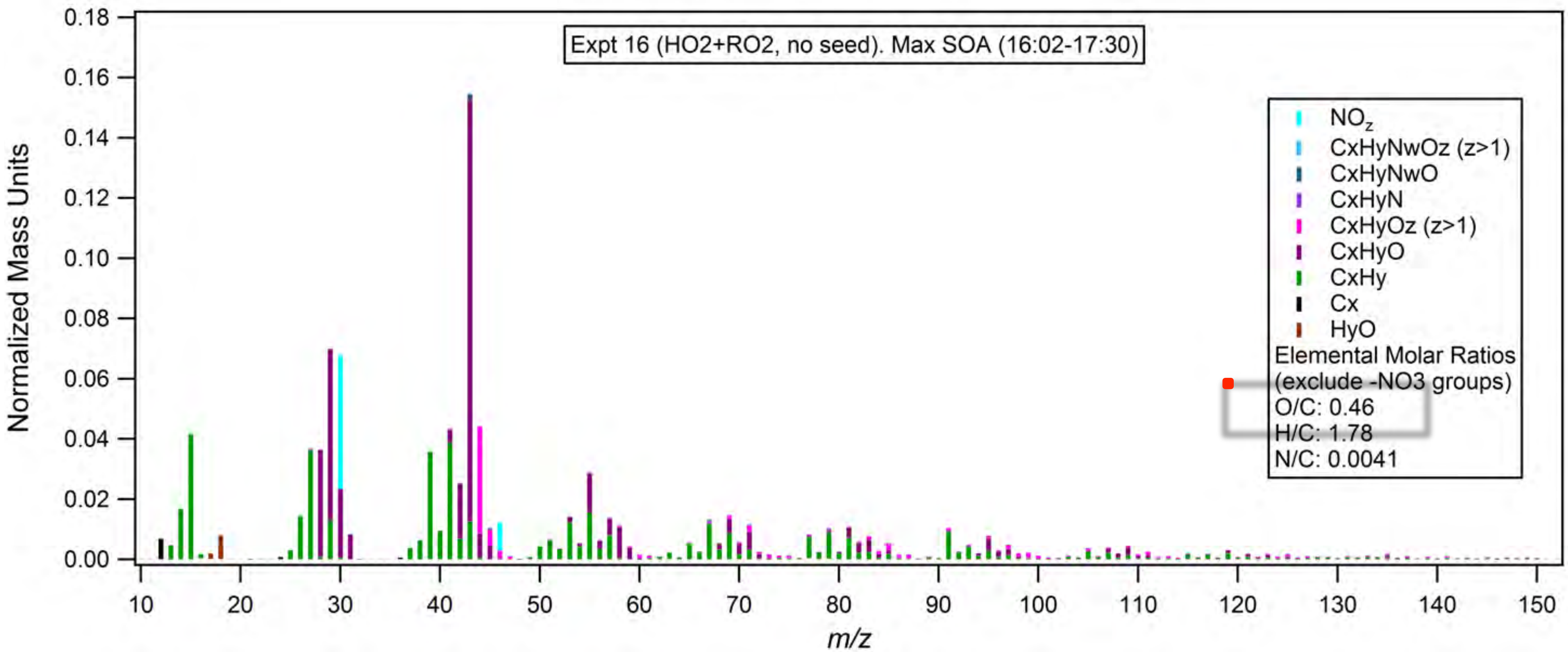


NO_3:Org: 0.18
(2*62/(812-2*62))

Chemical Formula: $C_{20}H_{32}N_2O_{32}$
Molecular Weight: 812.46

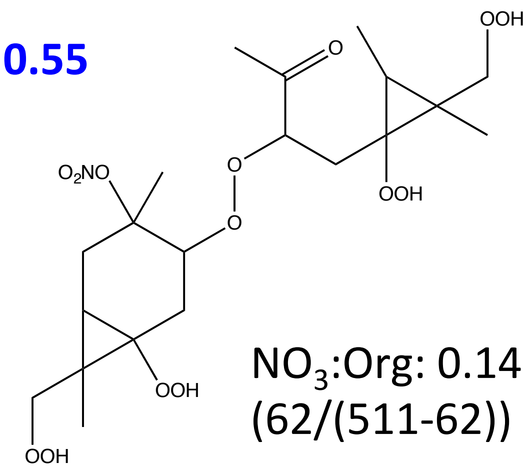
For this NO_3:Org ratio, need to either oxidize heavily or lose NO_2

Δ-carene chamber SOA composition clues



Average non-NO_3 O:C ratio suggests some NO_2 loss in condensing products

O:C = 0.55

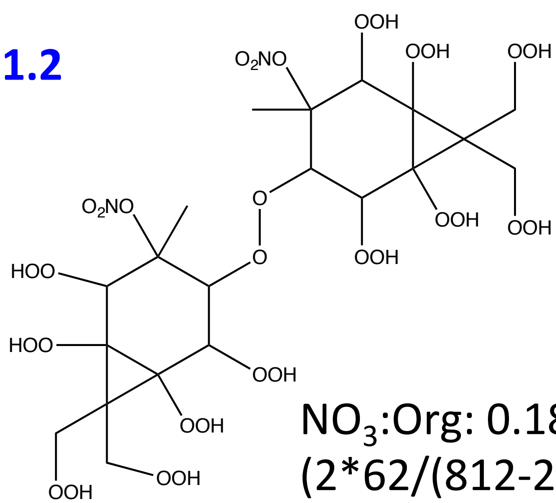


NO$_3$:Org: 0.14
(62/(511-62))

Chemical Formula: $C_{20}H_{33}NO_{14}$
Molecular Weight: 511.48

Observed O:C = 0.5

O:C = 1.2



NO$_3$:Org: 0.18
(2*62/(812-2*62))

Chemical Formula: $C_{20}H_{32}N_2O_{32}$
Molecular Weight: 812.46

Note: these O:C ratios all <u>exclude</u> the NO_3 groups

Conclusions

- NO_3 + BVOC is a significant contributor to SOA in various remote forests
- Most BVOC produce substantial SOA upon NO_3 oxidation; α-pinene does not
- This is likely due to α's lack of high-MW oxidation products
- α-pinene's exceptionalism is not simply a chamber artifact and is independent of RO_2 fate

Thanks!

- The best students & collaborators anyone could ask for: **Ben Ayres, Danielle Draper, Kang Kang**, Hannah Allen, Delphine Farmer, Yury Desyaterik, Doug Day, Jose Jimenez, Steve Brown

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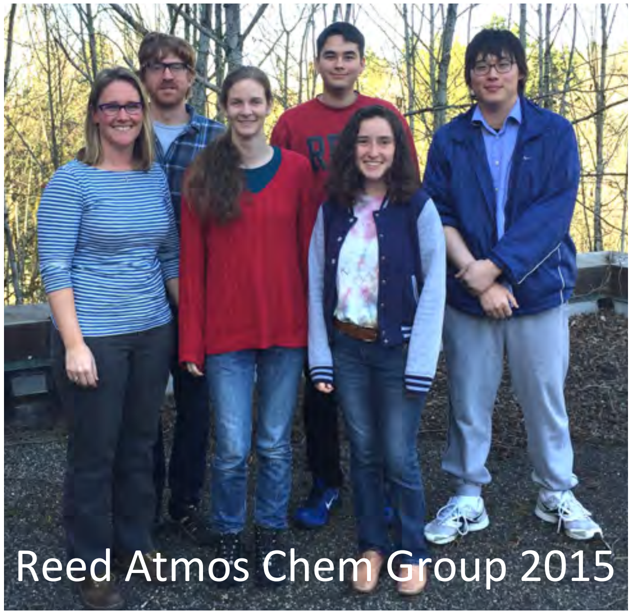
NOAA AC4 #NA13OAR4310070

Reed College Opportunity Grants

Reed SOAS 2013 team



Reed Atmos Chem Group 2015