

Nitrate radical initiated atmospheric particulate matter formation in forests:

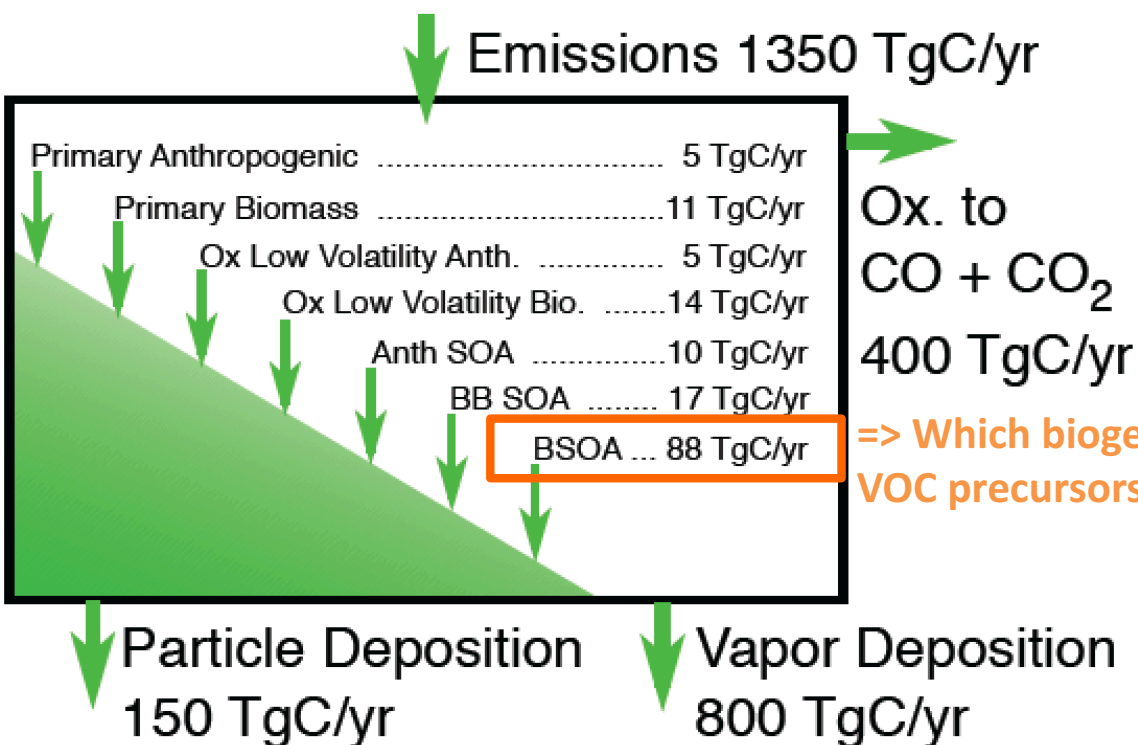
Anthropogenically-triggered biogenic aerosol production

Juliane L. Fry, Associate Professor of Chemistry & Environmental Studies, Reed College, Portland, OR
 SEAS, Harvard University, 2. Mar 2018

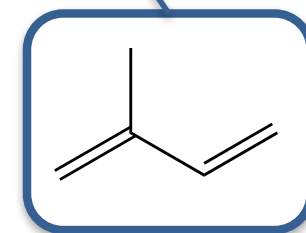
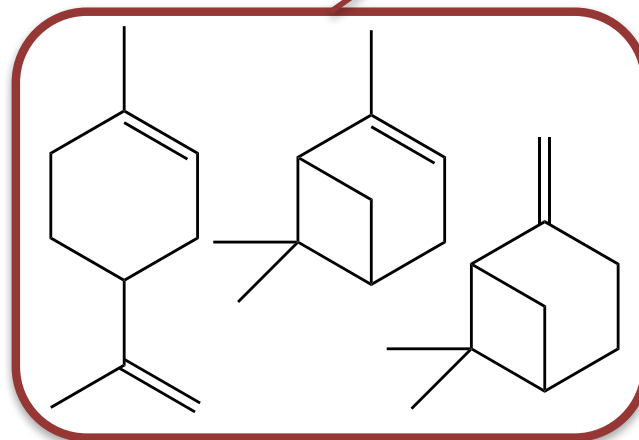
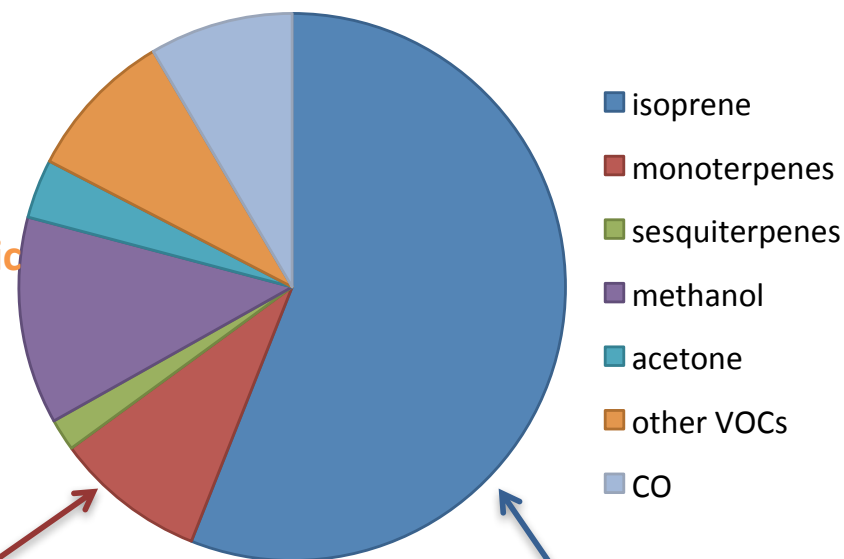
What's to come in this talk:

- Why do we think that NO_3 chemistry is an important contributor to secondary organic aerosol (SOA) formation?
- Two short stories about NO_3 + BVOC SOA formation:
 - Estimating SOA yields from **NO_3 + isoprene** based on nighttime aircraft power plant plume transects during SENEX 2013
 - Resolving the mystery of α -pinene's anomalously low NO_3 SOA yield with computational comparison of RO_2 fate from **NO_3 + α -pinene vs. NO_3 + Δ -carene**

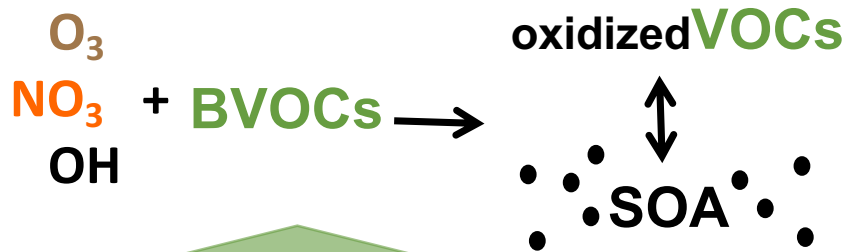
Global organic carbon budgets and biogenic SOA



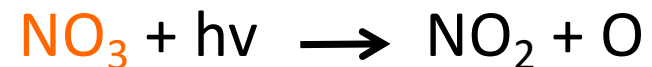
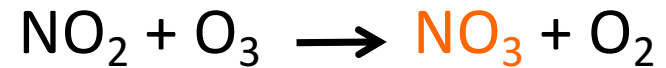
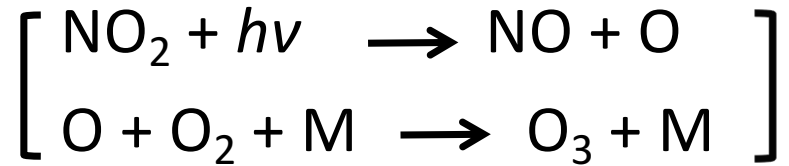
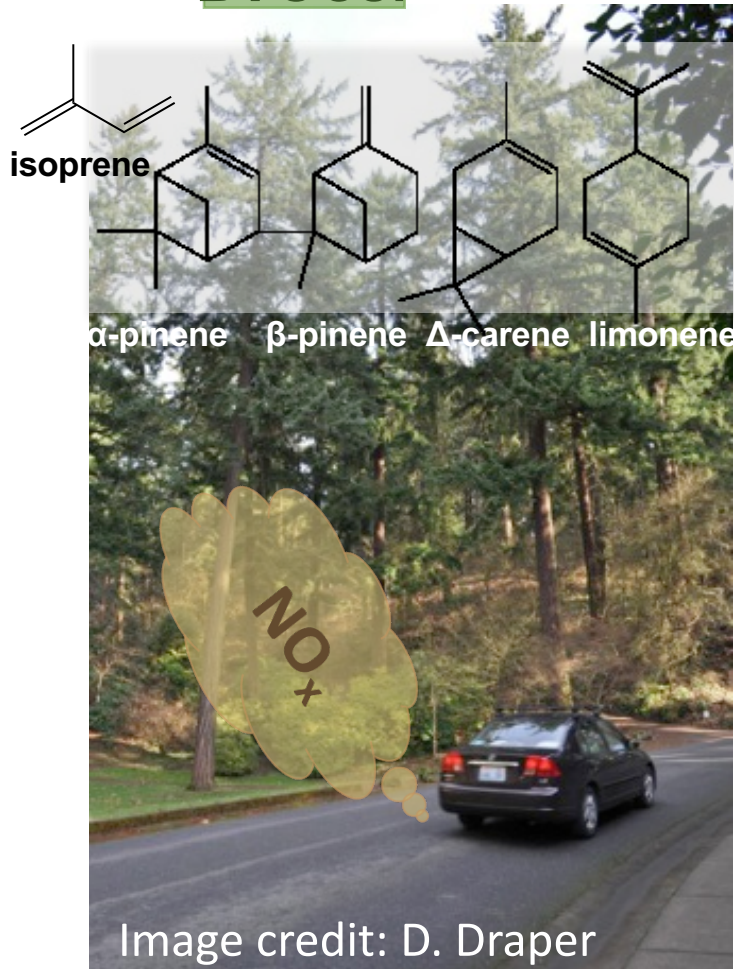
MEGAN model estimates 760 TgC yr⁻¹ global BVOC emissions, of which >60% is isoprene:



Oxidation of isoprene & monoterpenes (C₁₀ BVOCs)



BVOCs:



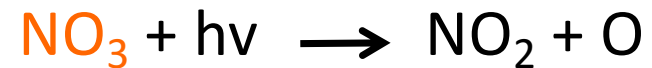
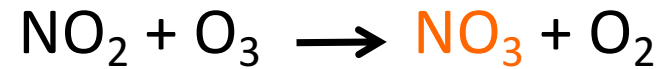
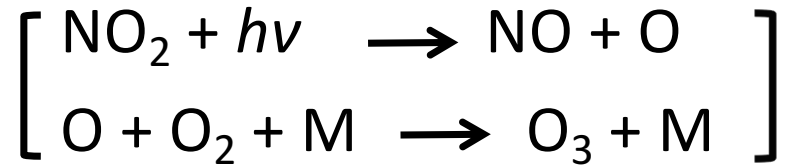
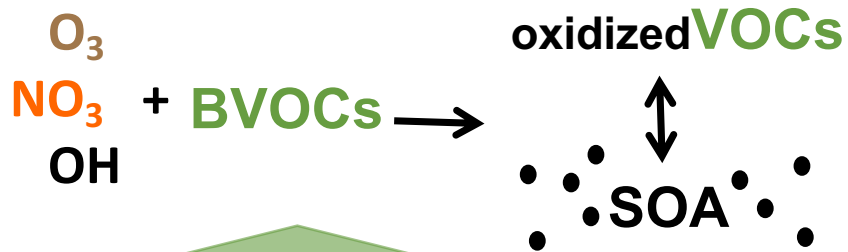
*NO₃ is rapidly photolyzed and thus active primarily at night

BVOC lifetimes w.r.t. each oxidant

BVOC	OH	O ₃	NO ₃
<i>isoprene</i>	1.4 hr	1.3 day	48 min
α-pinene	2.7 hr	4.7 hr	5.4 min
β-pinene	1.9 hr	1.1 day	13 min
Δ-carene	1.6 hr	11 hr	3.7 min
limonene	51 min	1.9 hr	2.7 min

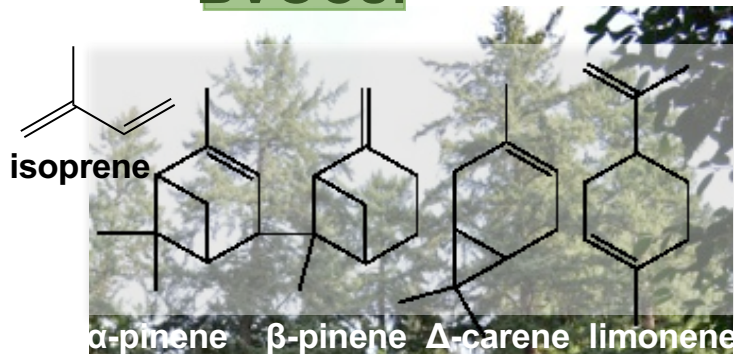
@ "typical" conc's: 12-h daytime avg [OH]: 2x10⁶ #/cm³; 24 h avg [O₃]: 7x10¹¹ #/cm³; 12 h nighttime avg [NO₃]: 5x10⁸ #/cm³ = 20 ppt (Atkinson & Arey, 2003)

Oxidation of isoprene & monoterpenes (C₁₀ BVOCs)



*NO₃ is rapidly photolyzed and thus active primarily at night

BVOCs:

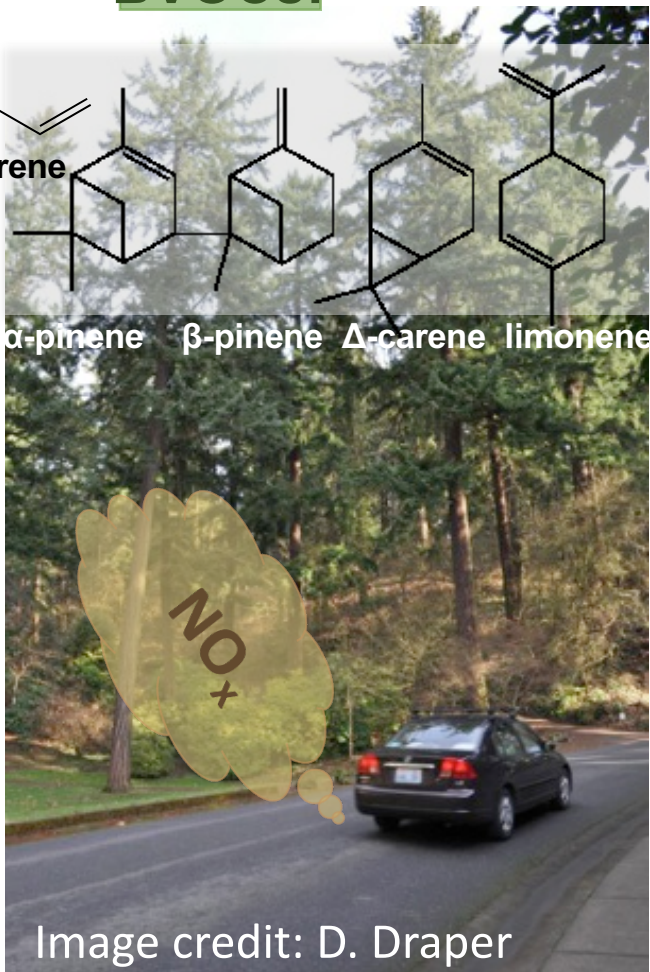


BVOC lifetimes w.r.t. each oxidant

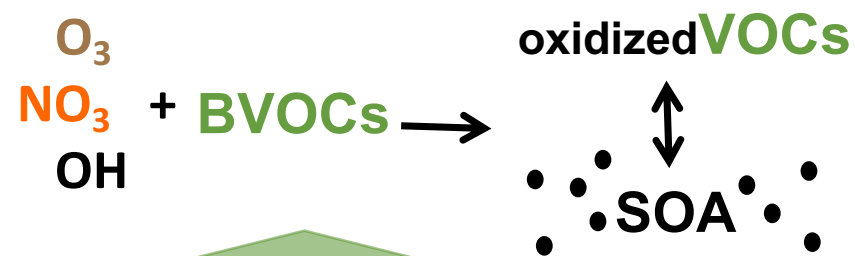
BVOC	OH	O ₃	NO ₃
<i>isoprene</i>	1.4 hr	1.3 day	48 min
α-pinene	2.7 hr	4.7 hr	5.4 min
β-pinene	1.9 hr	1.1 day	13 min
Δ-carene	1.6 hr	11 hr	3.7 min
limonene	51 min	1.9 hr	2.7 min

@ "typical" conc's: 12-h daytime avg [OH]: 2x10⁶ #/cm³; 24 h avg [O₃]: 7x10¹¹ #/cm³; 12 h nighttime avg [NO₃]: 5x10⁸ #/cm³ = 20 ppt (Atkinson & Arey, 2003)

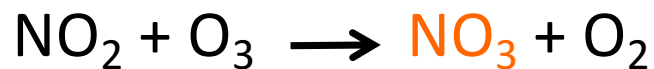
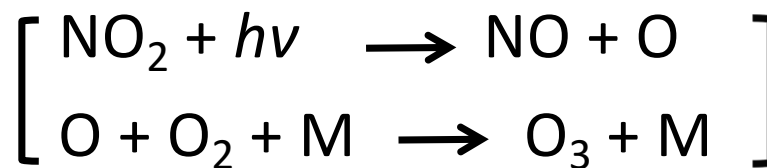
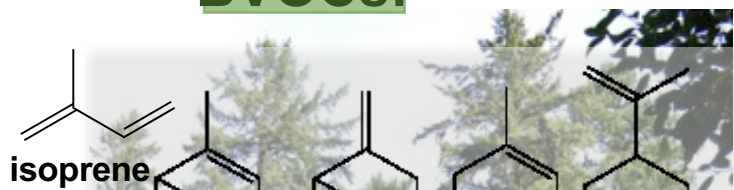
Image credit: D. Draper



SOA from isoprene & monoterpenes (C₁₀ BVOCs)



BVOCs:



*NO₃ is rapidly photolyzed and thus active primarily at night

BVOC lifetimes w.r.t. each oxidant

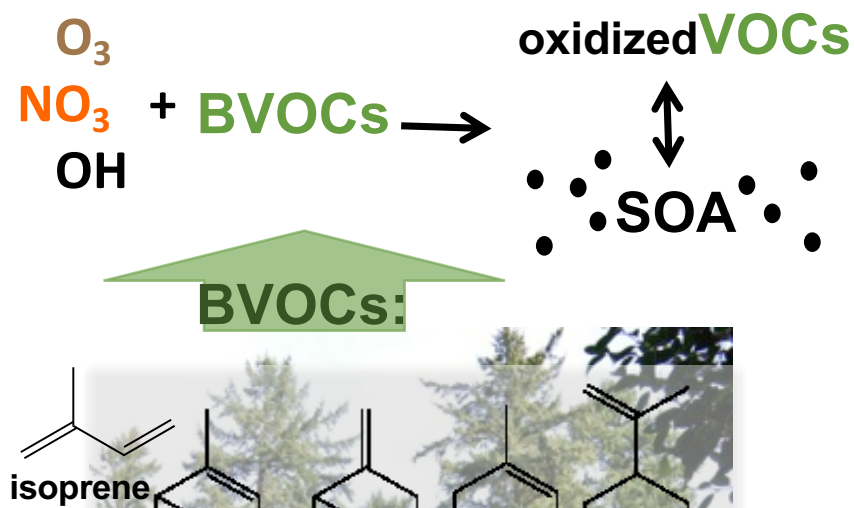
SOA yields (@ ~10 ug m⁻³)

BVOC	OH	O ₃	NO ₃	OH	O ₃	NO ₃
<i>isoprene</i>	1.4 hr	1.3 day	48 min	2% ^K	1% ^{KL}	10% ^{N,R}
α-pinene	2.7 hr	4.7 hr	5.4 min	8% ^E	10% ^S	0% ^{F14}
β-pinene	1.9 hr	1.1 day	13 min	3% ^G	20% ^{vH}	50% ^{F09}
Δ-carene	1.6 hr	11 hr	3.7 min	3% ^G	10% ^{G,Y}	50% ^{F14}
limonene	51 min	1.9 hr	2.7 min	9% ^G	40% ^L	40% ^{F11} 170% ^B

@ "typical" conc's: 12-h daytime avg [OH]: 2x10⁶ #/cm³; 24 h avg [O₃]: 7x10¹¹ #/cm³; 12 h nighttime avg [NO₃]: 5x10⁸ #/cm³ = 20 ppt (Atkinson & Arey, 2003)

^KKroll, EST 2006; ^EEddingsaas ACP 2012; ^GGriffin JGR 1999; ^YYu JAC 1999; ^{KL}Kleindienst, GRL 2006; ^SShilling, ACP 2008; ^{vH}von Hessberg, APC 2009; ^LLeungsakul ES&T 2009; ^NNg et al, ACP 2008; ^RRollins ACP 2009; ^{F09}Fry ACP 2009; ^{F11}Fry ACP 2011; ^{F14}Fry EST 2014; ^BBoyd et al., EST 2017

SOA from isoprene & monoterpenes (C₁₀ BVOCs)



Lab SOA yield studies:

- Conditions may not be representative of the real atmosphere (walls, no background OA, other radicals)
- Typically limited to < a few hours of SOA aging

*NO₃ is rapidly photolyzed and thus active primarily at night

BVOC lifetimes w.r.t. each oxidant

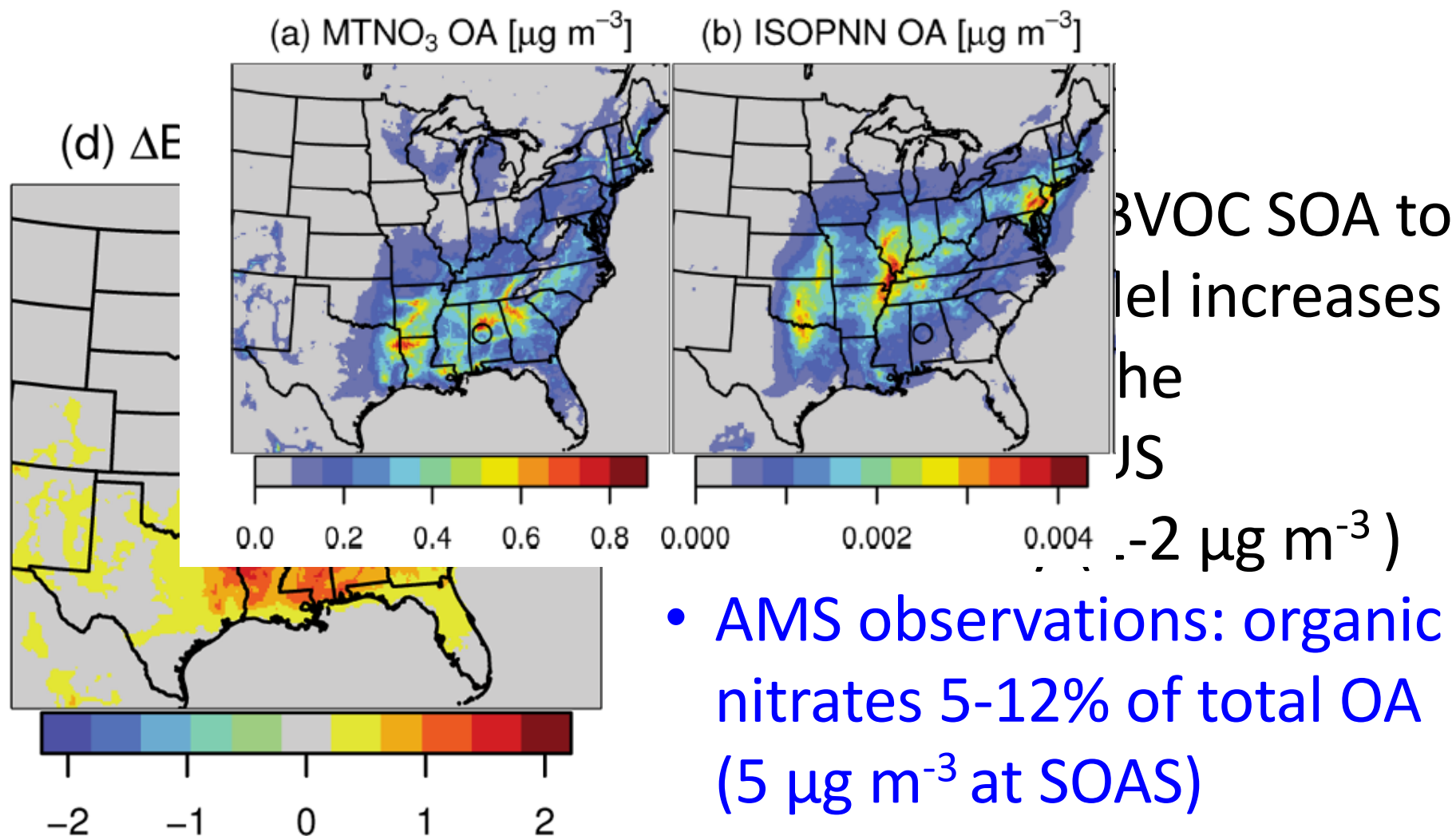
SOA yields (@ ~10 ug m⁻³)

BVOC	OH	O ₃	NO ₃	OH	O ₃	NO ₃
isoprene	1.4 hr	1.3 day	48 min	2% ^K	1% ^{KL}	10% ^{N,R}
α-pinene	2.7 hr	4.7 hr	5.4 min	8% ^E	10% ^S	0% ^{F14}
β-pinene	1.9 hr	1.1 day	13 min	3% ^G	20% ^{vH}	50% ^{F09}
Δ-carene	1.6 hr	11 hr	3.7 min	3% ^G	10% ^{G,Y}	50% ^{F14}
limonene	51 min	1.9 hr	2.7 min	9% ^G	40% ^L	40% ^{F11} 170% ^B

@ "typical" conc's: 12-h daytime avg [OH]: 2x10⁶ #/cm³; 24 h avg [O₃]: 7x10¹¹ #/cm³; 12 h nighttime avg [NO₃]: 5x10⁸ #/cm³ = 20 ppt (Atkinson & Arey, 2003)

^KKroll, EST 2006; ^EEddingsaas ACP 2012; ^GGriffin JGR 1999; ^YYu JAC 1999; ^{KL}Kleindienst, GRL 2006; ^SShilling, ACP 2008; ^{vH}von Hessberg, APC 2009; ^LLeungsakul ES&T 2009; ^NNg et al, ACP 2008; ^RRollins ACP 2009; ^{F09}Fry ACP 2009; ^{F11}Fry ACP 2011; ^{F14}Fry EST 2014; ^BBoyd et al., EST 2017

Regional modeling & organonitrate aerosol observations show NO_3 oxidation is an important source of SOA

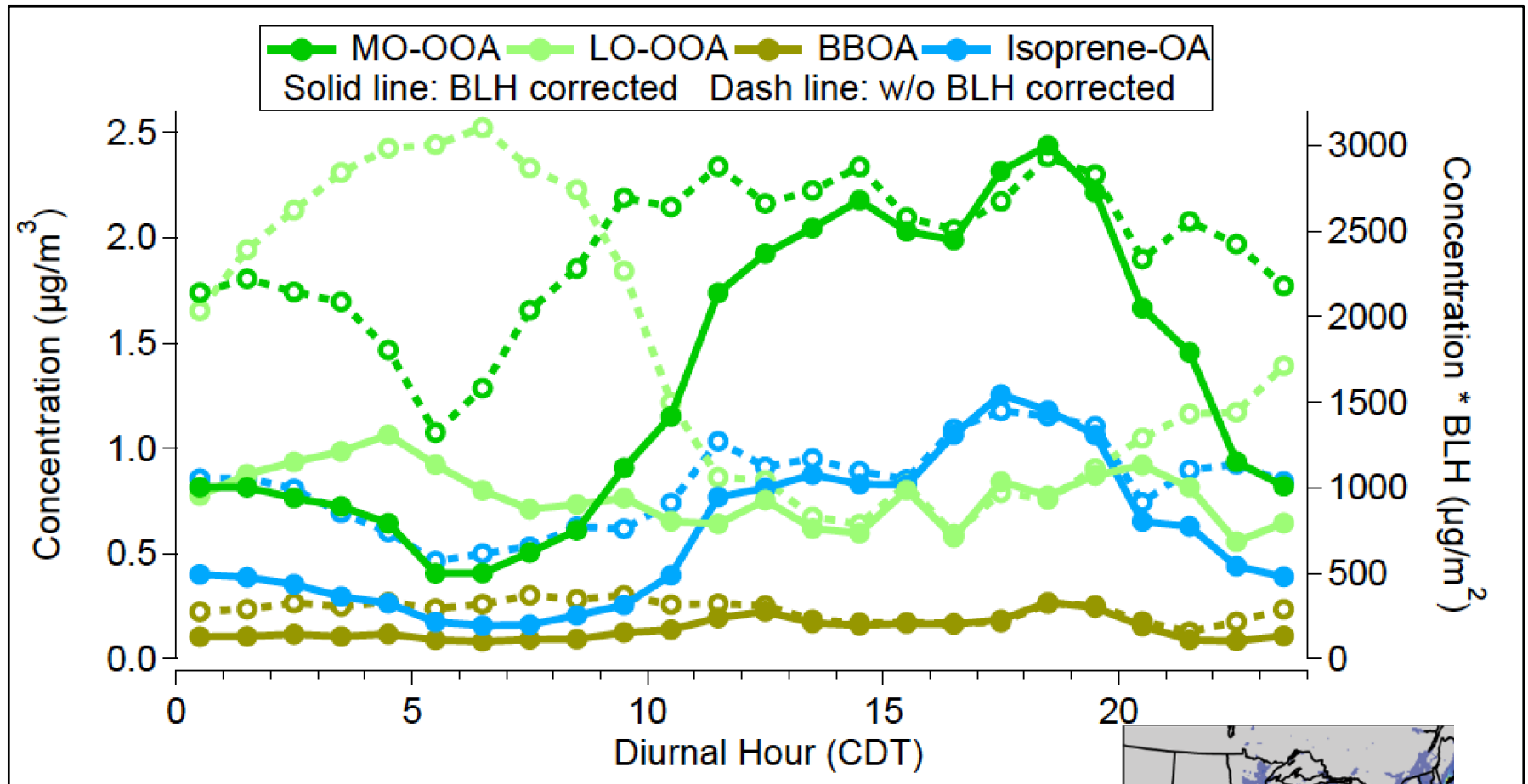


BVOC SOA to
 el increases
 he
 JS
 .-2 $\mu\text{g m}^{-3}$)

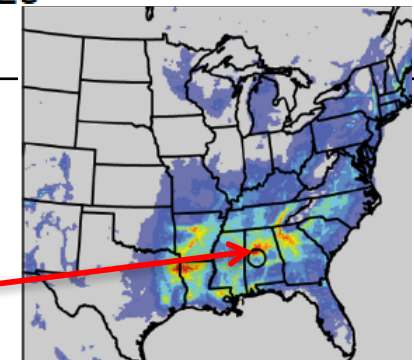
- AMS observations: organic nitrates 5-12% of total OA (5 $\mu\text{g m}^{-3}$ at SOAS)

=> Which BVOCs? Monoterpenes / isoprene?

Can diurnal patterns in AMS factors give clues about SOA sources?



Data from **SOAS ground site**, Xu et al., PNAS 2015

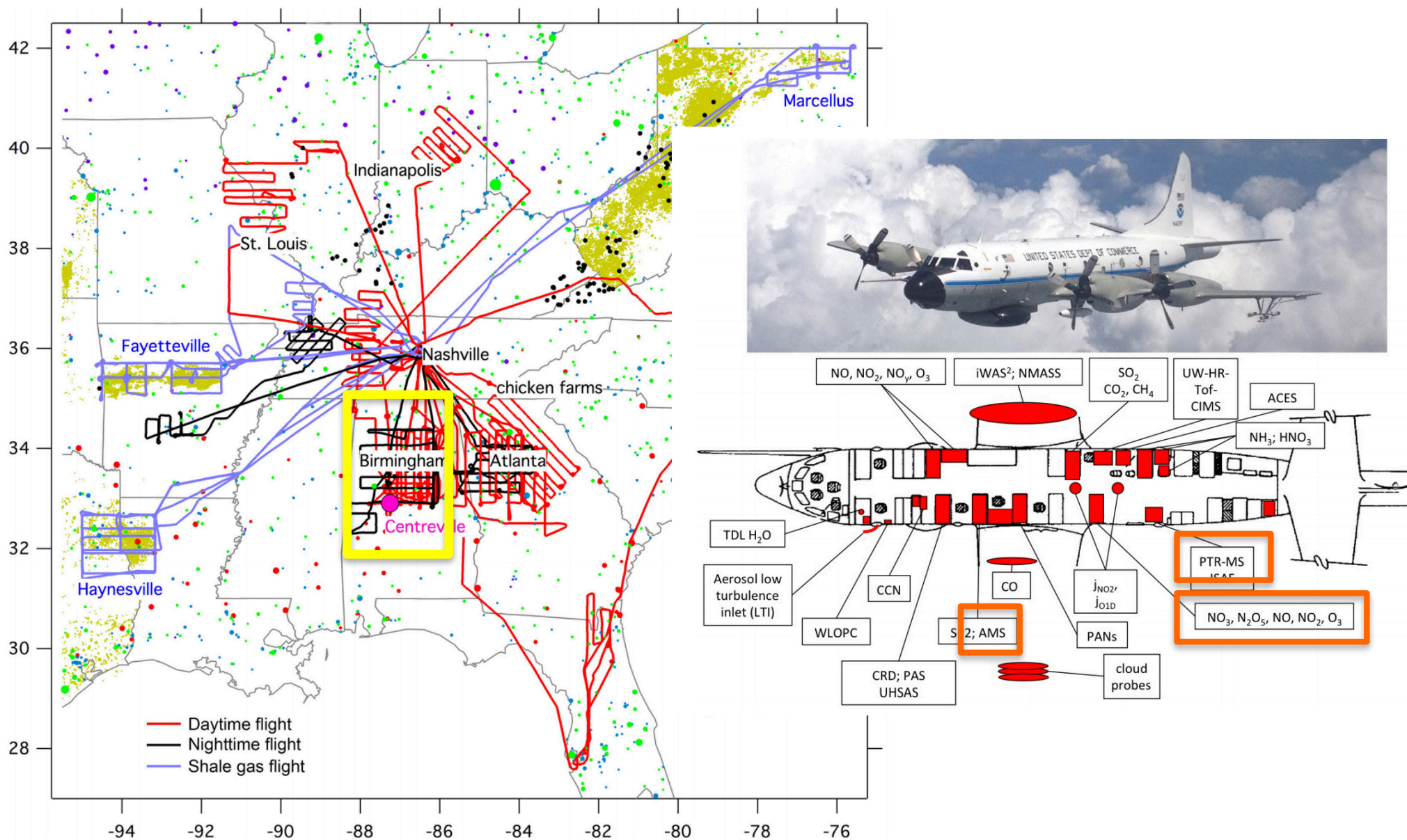


Short story #1: Assess NO_3 + isoprene SOA yield from aircraft measurements in regions of rapid NO_3 oxidation of isoprene: power plant plumes



Gorgas steam plant, Parrish, Alabama

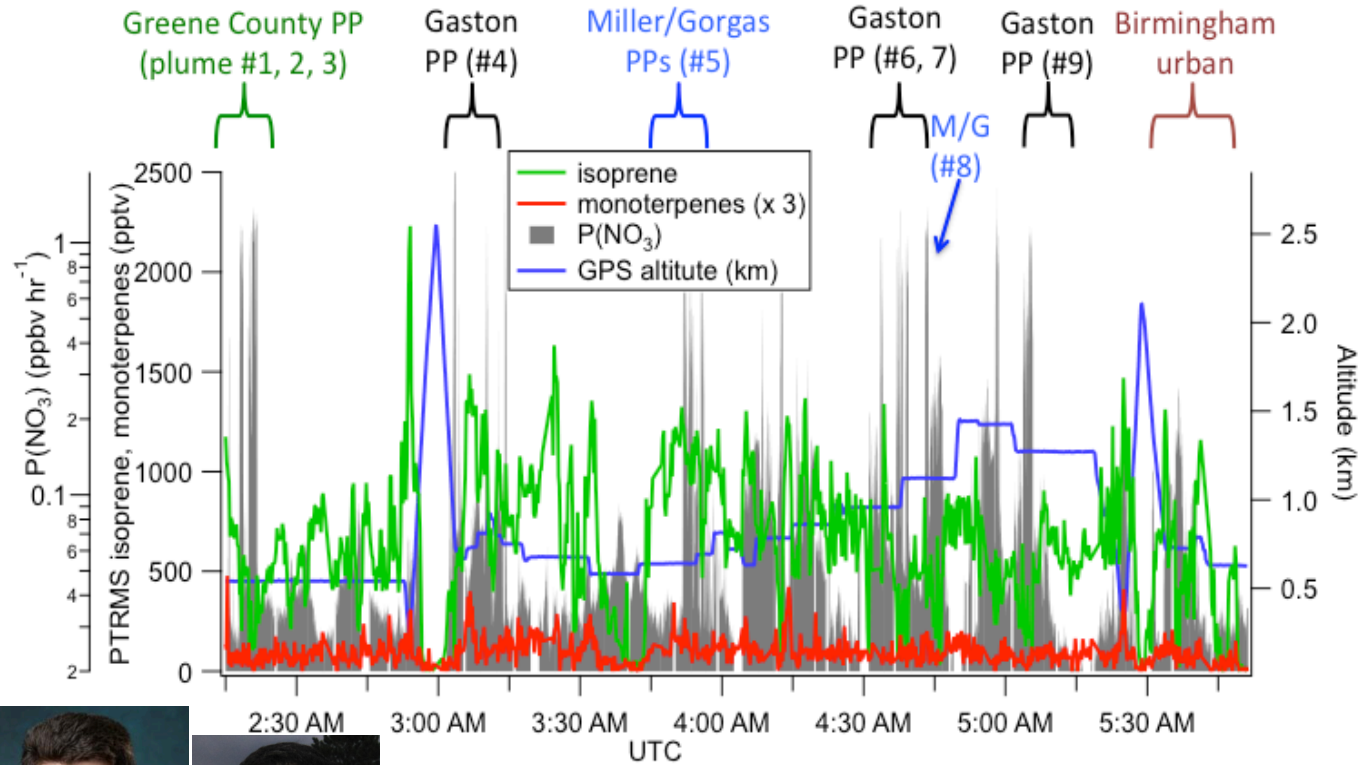
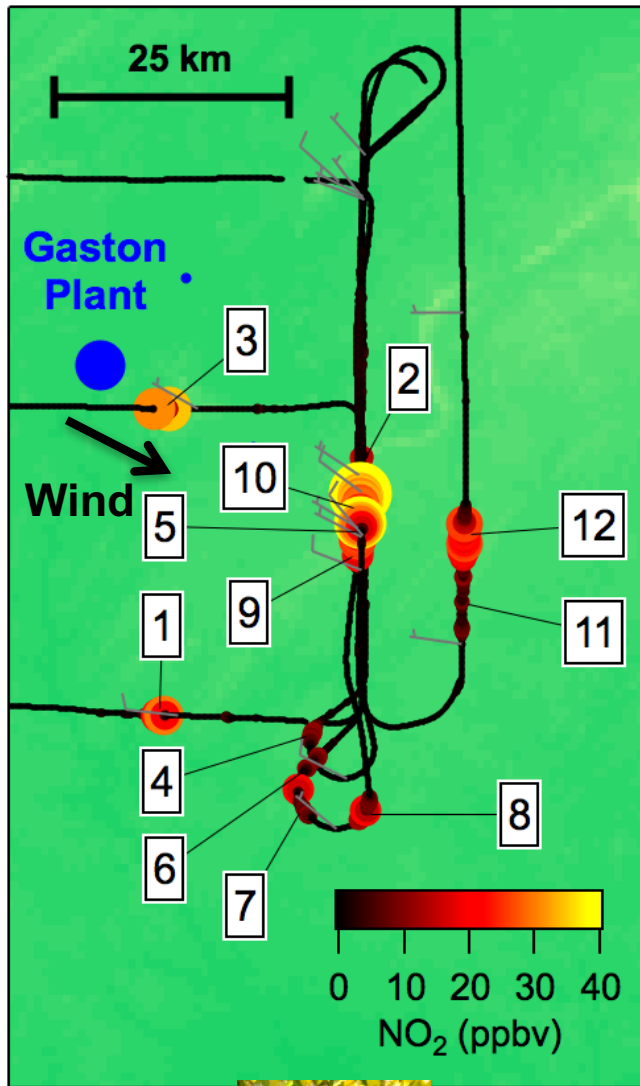
SENEX 2013: 21 research flights



Power plant plume transects during July 2, 2013 night flight

- Power plants are largest source of residual layer NO_x
- BVOC are titrated in narrow, concentrated plumes:

$$P_{\text{NO}_3} = k_{\text{NO}_2+\text{O}_3}(T) [\text{NO}_2][\text{O}_3]$$



(subset of flight)



Pete Edwards



Steve Brown



Ann Middlebrook

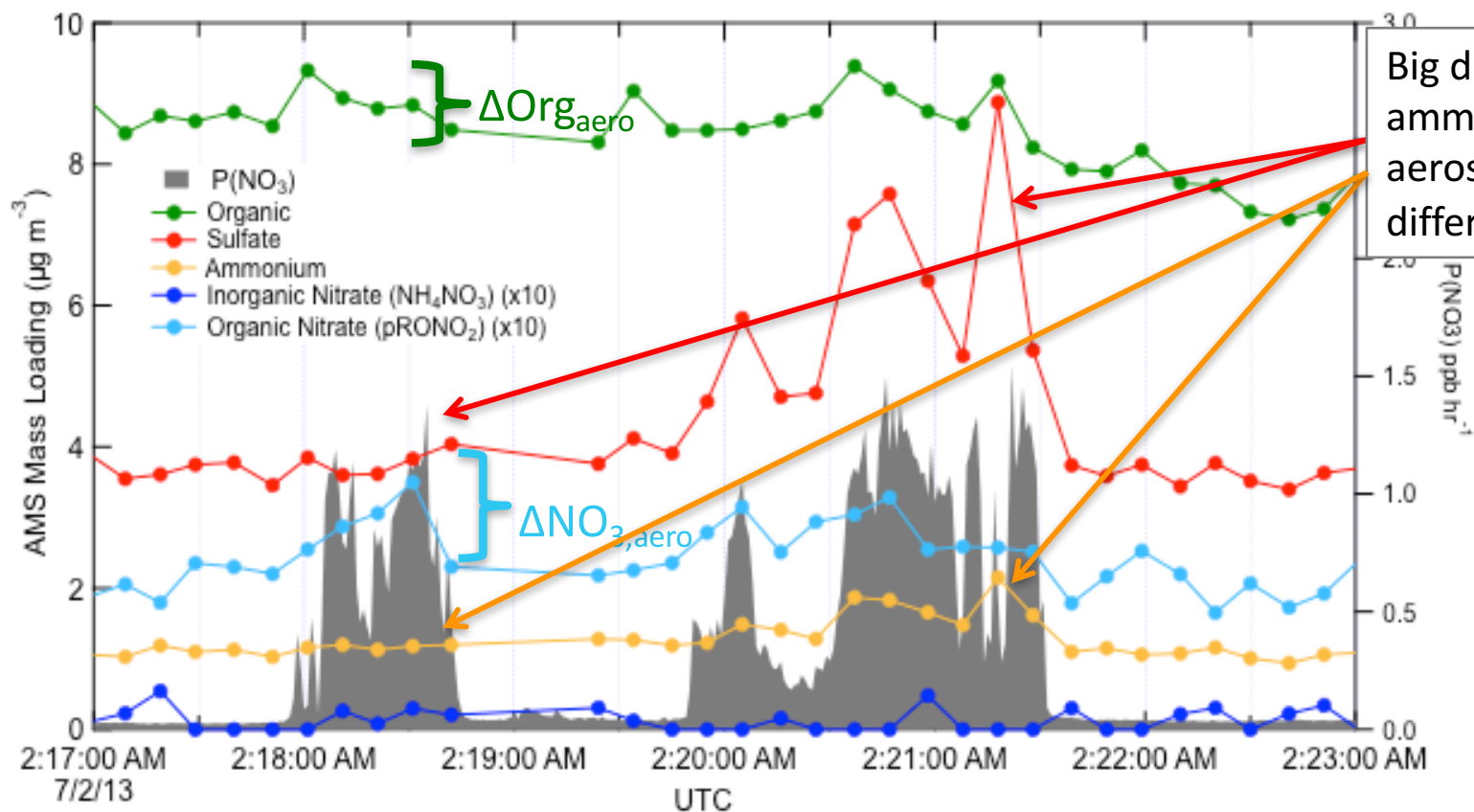
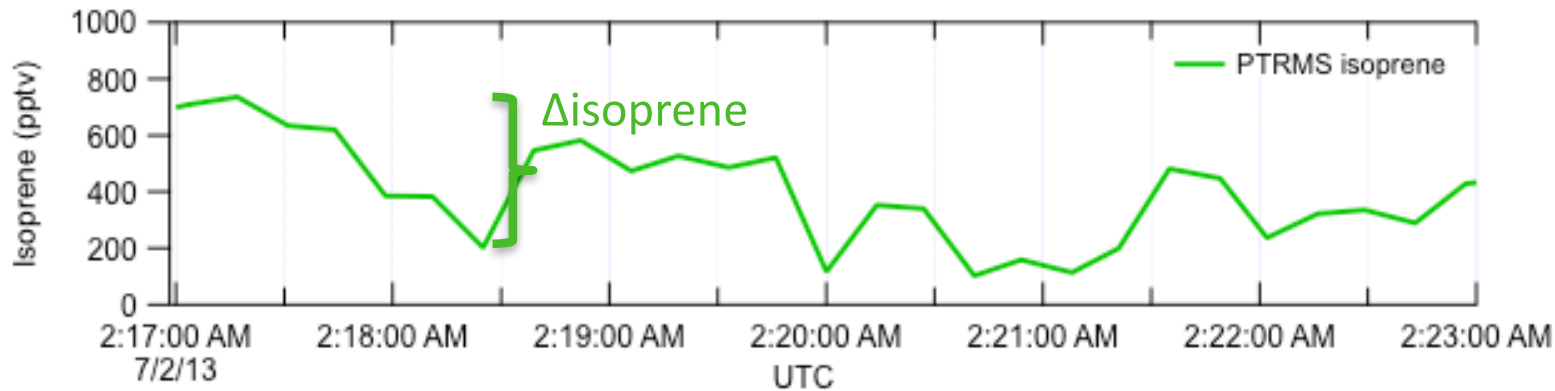


Jose Jimenez



Doug Day

Aircraft plume transects



Big differences in ammonium and sulfate aerosol produced in different plumes.

Screening plumes: Verify that aerosol increases were produced only by NO_3 + isoprene

(1) is all of the **NO_3 reactivity** in plumes due to reaction with isoprene?

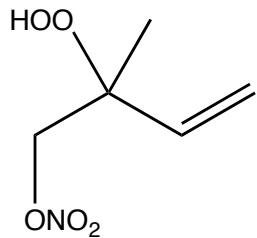
✓ Based on observed isoprene: monoterpene ratio and known rate constants, yes.

(2) is all of the change in **aerosol organic mass concentration** during these plumes due to NO_3 + isoprene reactions?

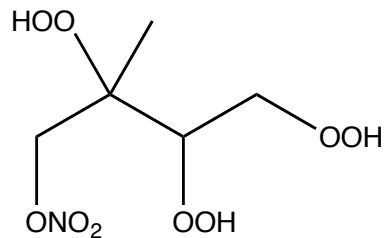
(1) is all of the change in **aerosol nitrate mass concentration** due to NO_3 + isoprene reactions?

(2) is all of the change in aerosol organic mass concentration during these plumes due to NO_3 + isoprene reactions?

- Organic:nitrate mass increase ratio in plumes is noisy, avg ~ 5
- What kind of isoprene organic nitrate molecular structure would have this Org: NO_3 ratio?

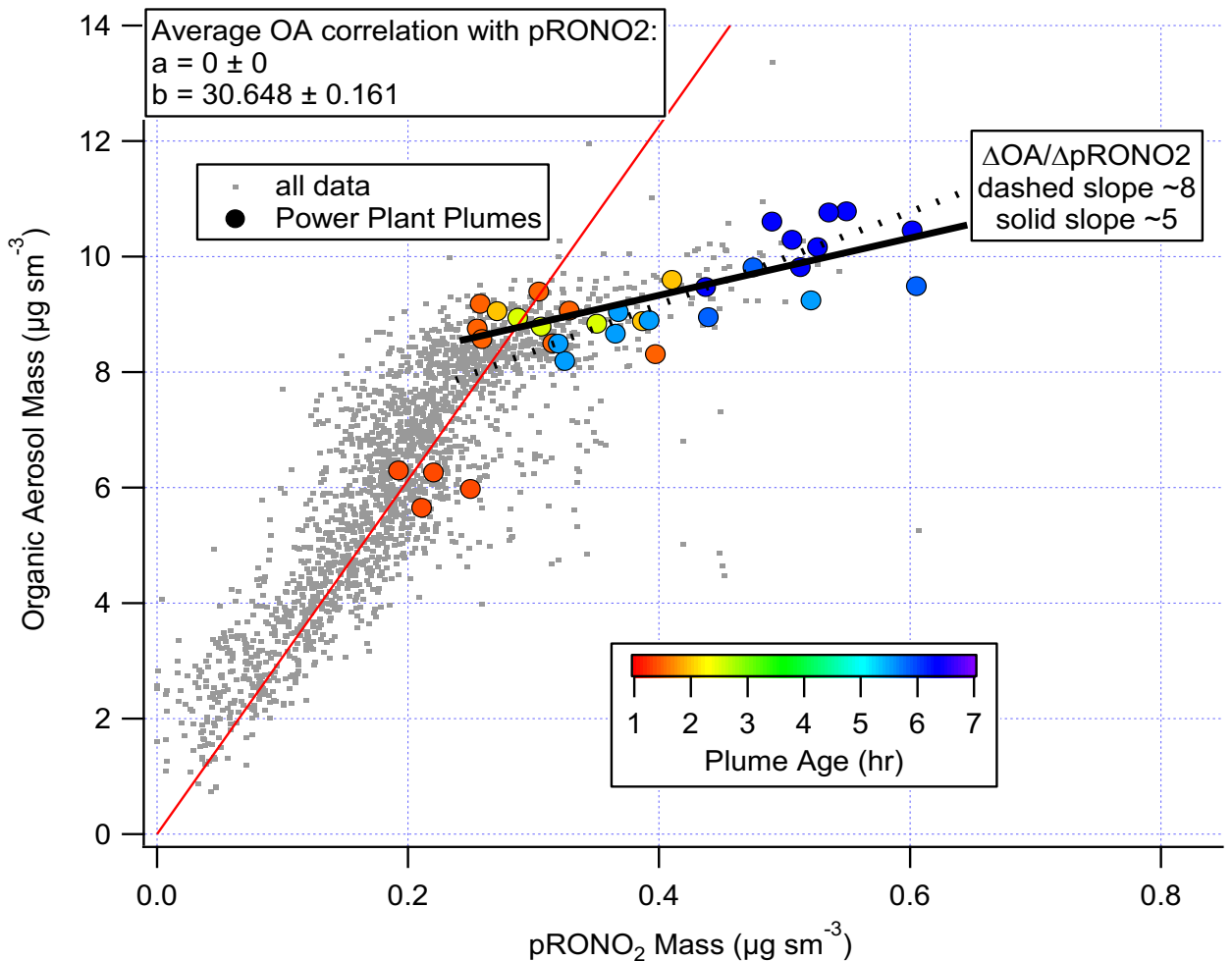


Org: NO_3 = 1.6



Org: NO_3 = 2.7

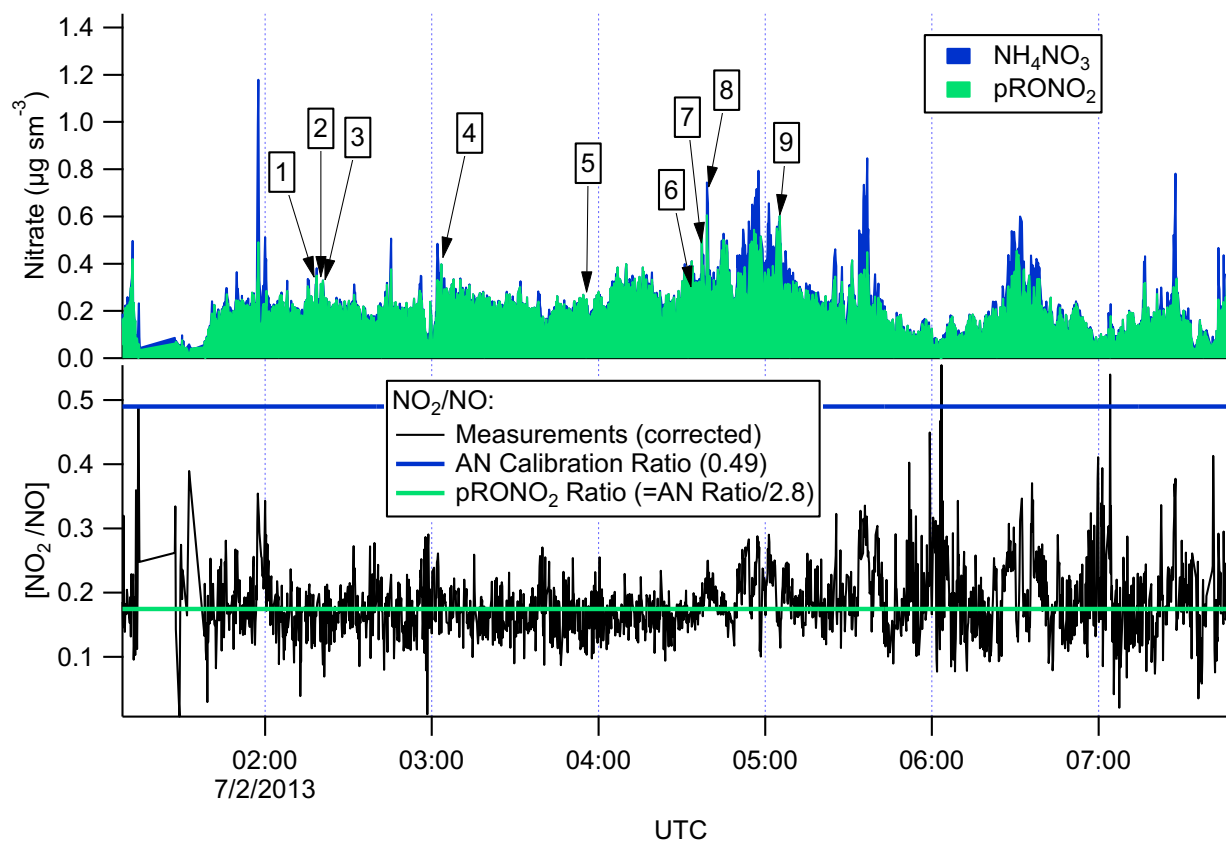
- \Rightarrow Would need 10 (!) more O's on this molecule to get Org: NO_3 to 5!
- \Rightarrow Or, co-condensing organics? Loss of NO_3 functional groups?



Screening plumes: Verify that aerosol increases were produced only by NO_3 + isoprene

- (1) is all of the **NO_3 reactivity** in plumes due to reaction with isoprene? ✓ Based on observed isoprene: monoterpene ratio and known rate constants, yes.
- (2) is all of the change in **aerosol organic mass concentration** during these plumes due to NO_3 + isoprene reactions? ✗ Based on very high Org: NO_3 ratios and correlation with total aerosol mass, likely other organics contribute
- (1) is all of the change in **aerosol nitrate mass concentration** due to NO_3 + isoprene reactions?

(3) is all of the change in **aerosol nitrate mass concentration** due to NO_3 + isoprene reactions?



Previous studies report $\text{NO}_2^+:\text{NO}^+$ ratios for organic nitrates typically 2–3 times lower than for NH_4NO_3 (Fry et al., 2009, 2011; Bruns et al., 2010; Farmer et al., 2010; Liu et al., 2012); this can be used to apportion organic (pRONO_2) vs. inorganic (NH_4NO_3) nitrate. **Conclusion: no sign of significant inorganic nitrate interference in plumes.**

Screening plumes: Verify that aerosol increases were produced only by NO₃ + isoprene

(1) is all of the **NO₃ reactivity** in plumes due to reaction with isoprene?

✓ Based on observed isoprene: monoterpene ratio and known rate constants, yes.

(2) is all of the change in **aerosol organic mass concentration** during these plumes due to NO₃ + isoprene reactions?

✗ Based on absurd Org:NO₃ ratios and correlation with aerosol mass, likely other organics contribute

(1) is all of the change in **aerosol nitrate mass concentration** due to NO₃ + isoprene reactions?

✓ Based on NO⁺:NO₂⁺ ratios, all increase is organic nitrate (& pRONO₂ is separable)

So, we will calculate SOA mass yields as:

$$Y_{SOA, mass} = \frac{(pRONO2_{plume} \pm SD_{pRONO2plume}) - (pRONO2_{bkg} \pm SD_{pRONO2bkg})}{-[(isop_{plume} \pm SD_{isopplume}) - (isop_{bkg} \pm SD_{isopbkg})]} \times 3 \times \frac{329ppt}{\mu g m^{-3}}$$

3: nitrate mass + associated organics, assumed to be approximately double the nitrate mass.
Requires ~4 additional oxygens: e.g. a tri-hydroperoxynitrate

Observed SOA yields are large; higher at longest plume ages

plume number	plume time (UTC)	SOA molar yield (fraction) [± SD]	SOA mass yield (fraction) [± SD]	plume age from O ₃ /NO ₂ clock assuming S=1 (hours)	Likely NO _x origin & altitude (m)
1	7/2/13 2:18	0.09 [0.05]	0.25 [0.14]	2.5	Greene County @ 540 m
2	7/2/13 2:20	0.07	0.21	1.5	<i>ibid</i>
3	7/2/13 2:21	0.12 [0.10]	0.32 [0.27]	1.5	<i>ibid</i>
4	7/2/13 3:03	0.13	0.36	1.5	Gaston @ 720 m
5	7/2/13 3:55	0.06 [0.07]	0.17 [0.20]	1.4	Miller / Gorgas @ 690 m
6	7/2/13 4:34	0.05 [0.02]	0.15 [0.07]	2	<i>ibid</i>
7	7/2/13 4:37	0.10 [0.11]	0.26 [0.31]	5.5	<i>ibid</i>
8	7/2/13 4:39	0.16 [0.10]	0.45 [0.26]	5.8	Miller / Gorgas @ 1120 m
9	7/2/13 5:04	0.28 [0.14]	0.77 [0.39]	6.3	Gaston @ 1280 m

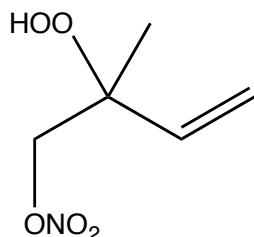
Chamber-based SOA mass yield estimates: 12-14% (Ng et al., 2008; Rollins et al., 2009)

Plume age estimates based on O₃/NO₂ ratio clock and model

=> What yield number *should* be used in models?

What isoprene products are likely contributing to SOA?

Likely 1st-generation product:



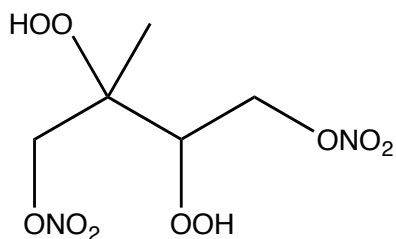
Based on ground contribution method (Pankow & Asher, 2008) P_{vap} , predicted C^* :

$$2.5 \times 10^4 \mu\text{g m}^{-3}$$

O:C elemental ratio (excluding NO_3):

0.4

Possible 2nd-generation products:

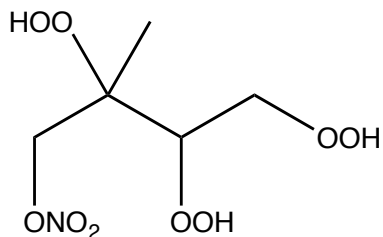


$$0.38 \mu\text{g m}^{-3}$$

This suggests that 1st generation products cannot contribute, but 2nd-gen can
 No oligomerization required

0.8

Or:

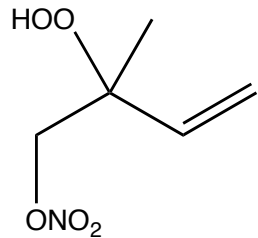


$$0.20 \mu\text{g m}^{-3}$$

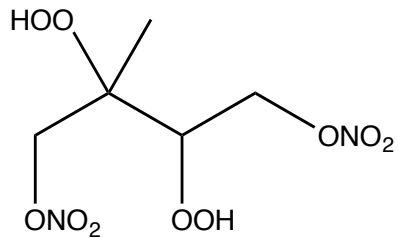
1.2

Could NO_3 +isoprene products be a significant contributor @ surface?

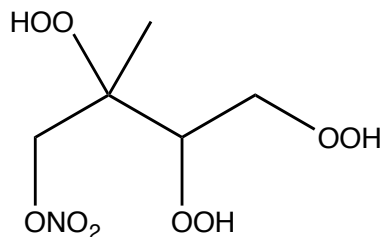
O:C elemental ratio (excluding NO_3):



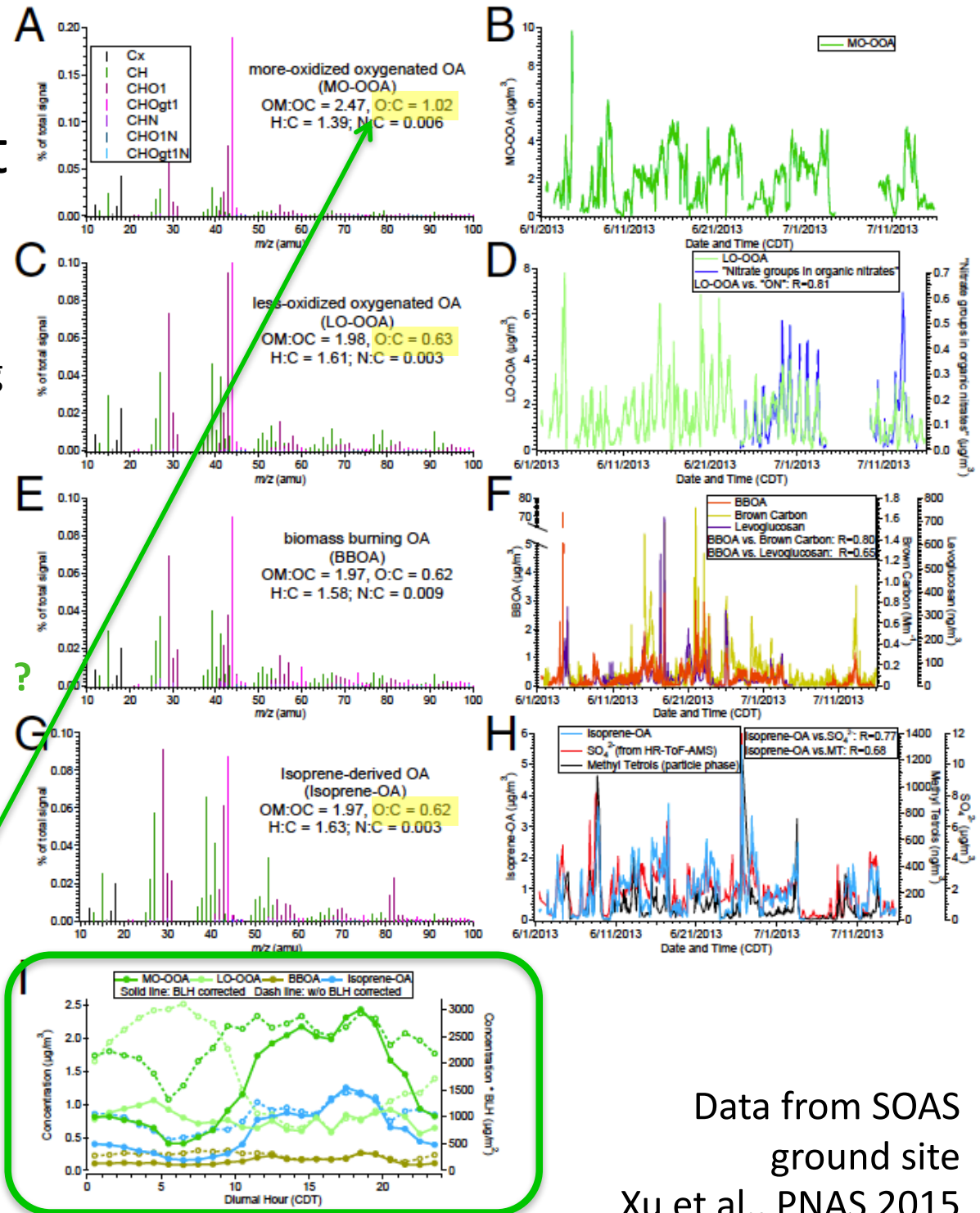
0.4



0.8



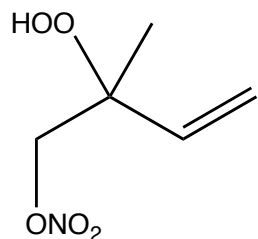
1.2



Data from SOAS ground site
Xu et al., PNAS 2015

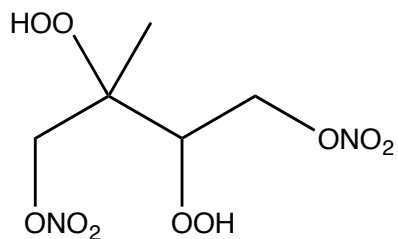
Could NO₃+isoprene products be a significant contributor to organic aerosol at the surface?

MO-OOA was 39% of total OA at SOAS
 And it sure looks like an isoprene product

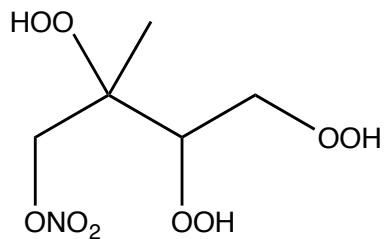


O:C elemental ratio (excluding NO₃):

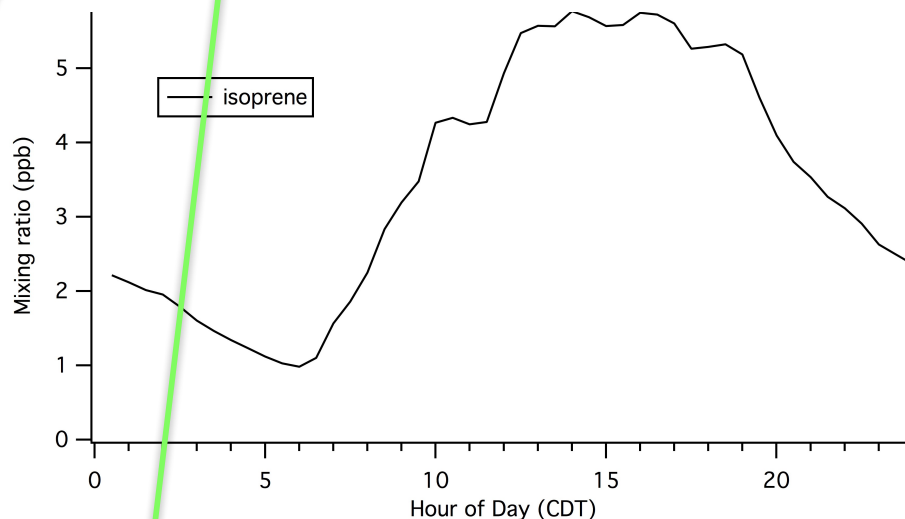
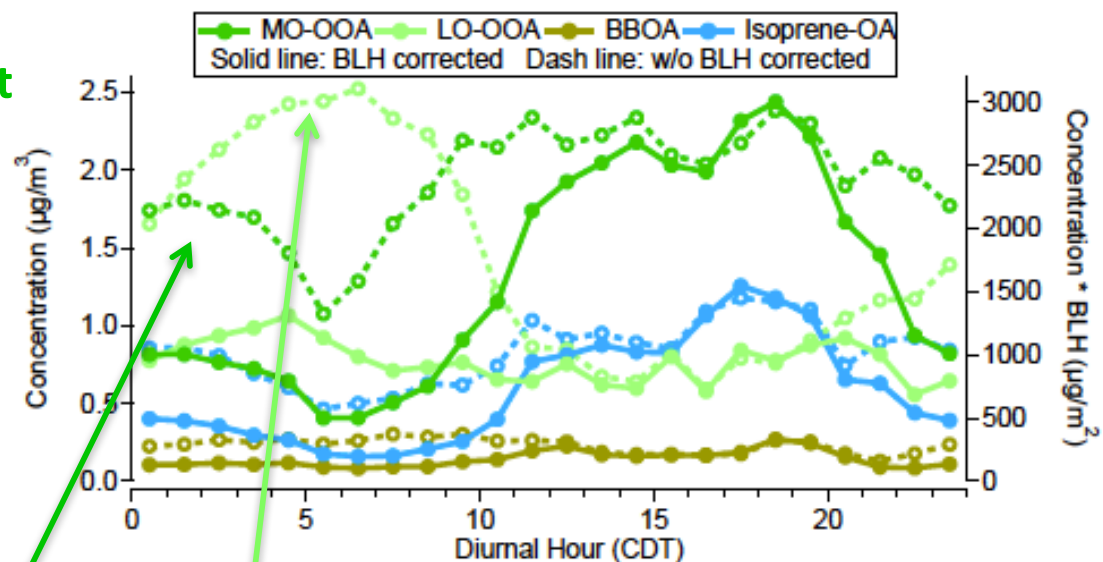
0.4



0.8



1.2



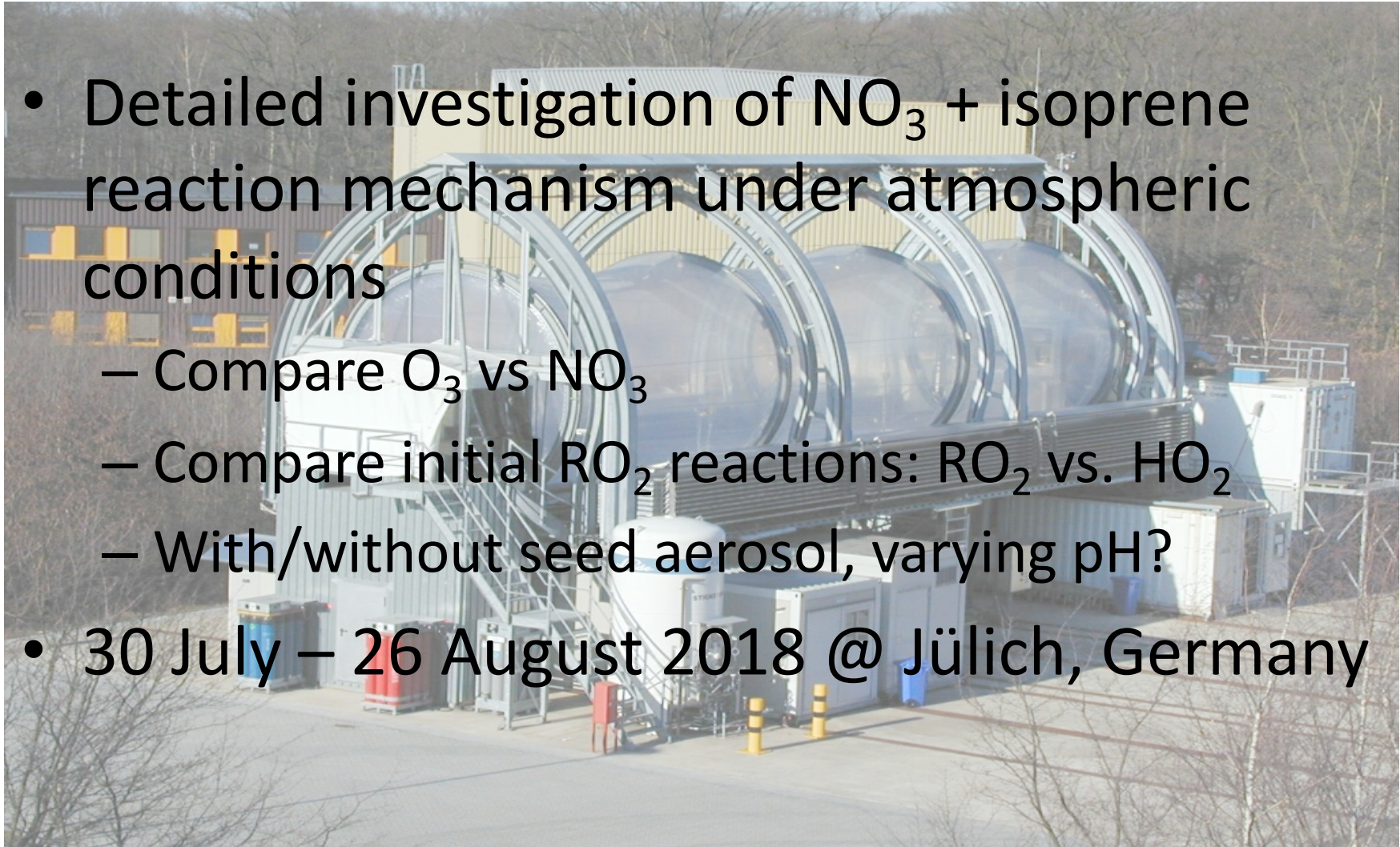
Xu et al. speculated that LO-OOA factor was due to NO₃+ terpene products @ SOAS

Conclusions about NO_3 + isoprene SOA yields

- NO_3 + isoprene yields assessed from aircraft measurements increased with plume age, to as much as 10x (!) the typically assumed yield in models
- This reaction may contribute substantially to an identified organic aerosol factor comprising 40% of total OA at the surface (measured at the SOAS ground site in central Alabama)
- In warm, rapidly industrializing regions of the world where isoprene emissions are large and NO_x emissions are on the rise (e.g. parts of China, India), this SOA source may be increasing

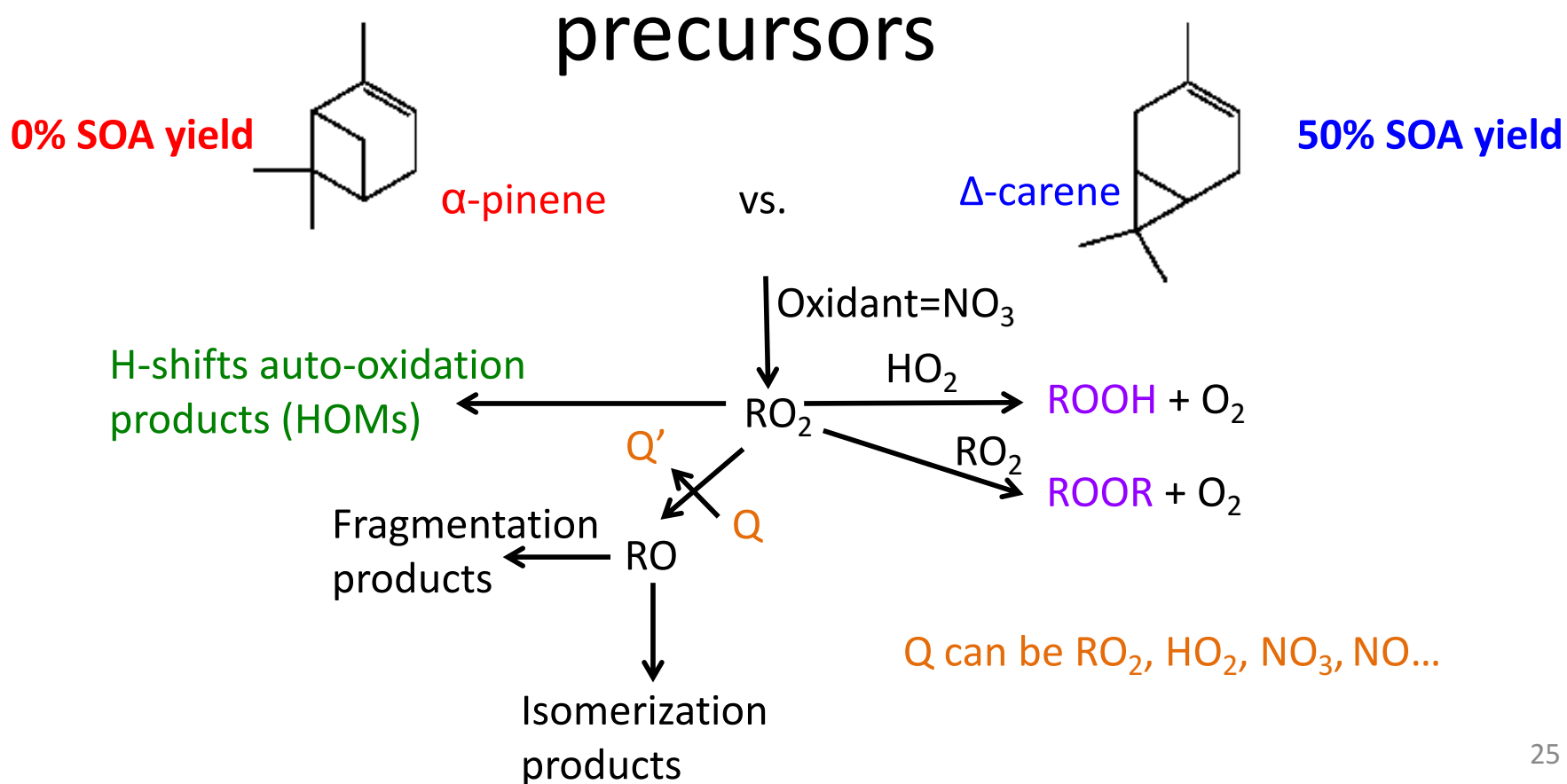
Plans for summer 2018 SAPHIR chamber NO_3 + isoprene SOA study

- Detailed investigation of NO_3 + isoprene reaction mechanism under atmospheric conditions
 - Compare O_3 vs NO_3
 - Compare initial RO_2 reactions: RO_2 vs. HO_2
 - With/without seed aerosol, varying pH?
- 30 July – 26 August 2018 @ Jülich, Germany



Short story #2: What about SOA produced from NO_3 + monoterpenes?

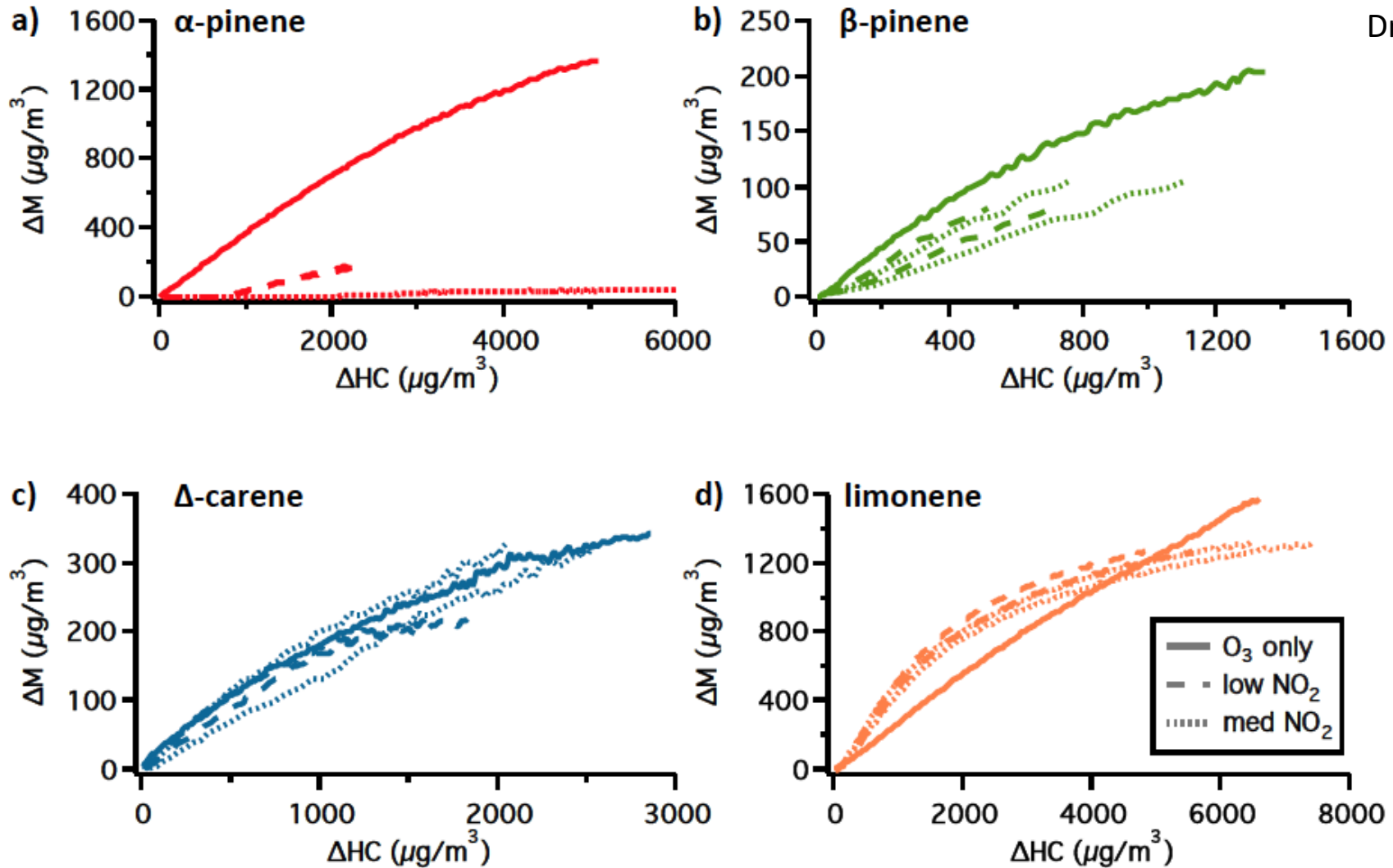
A puzzle about large differences in SOA yield for very similar looking monoterpene



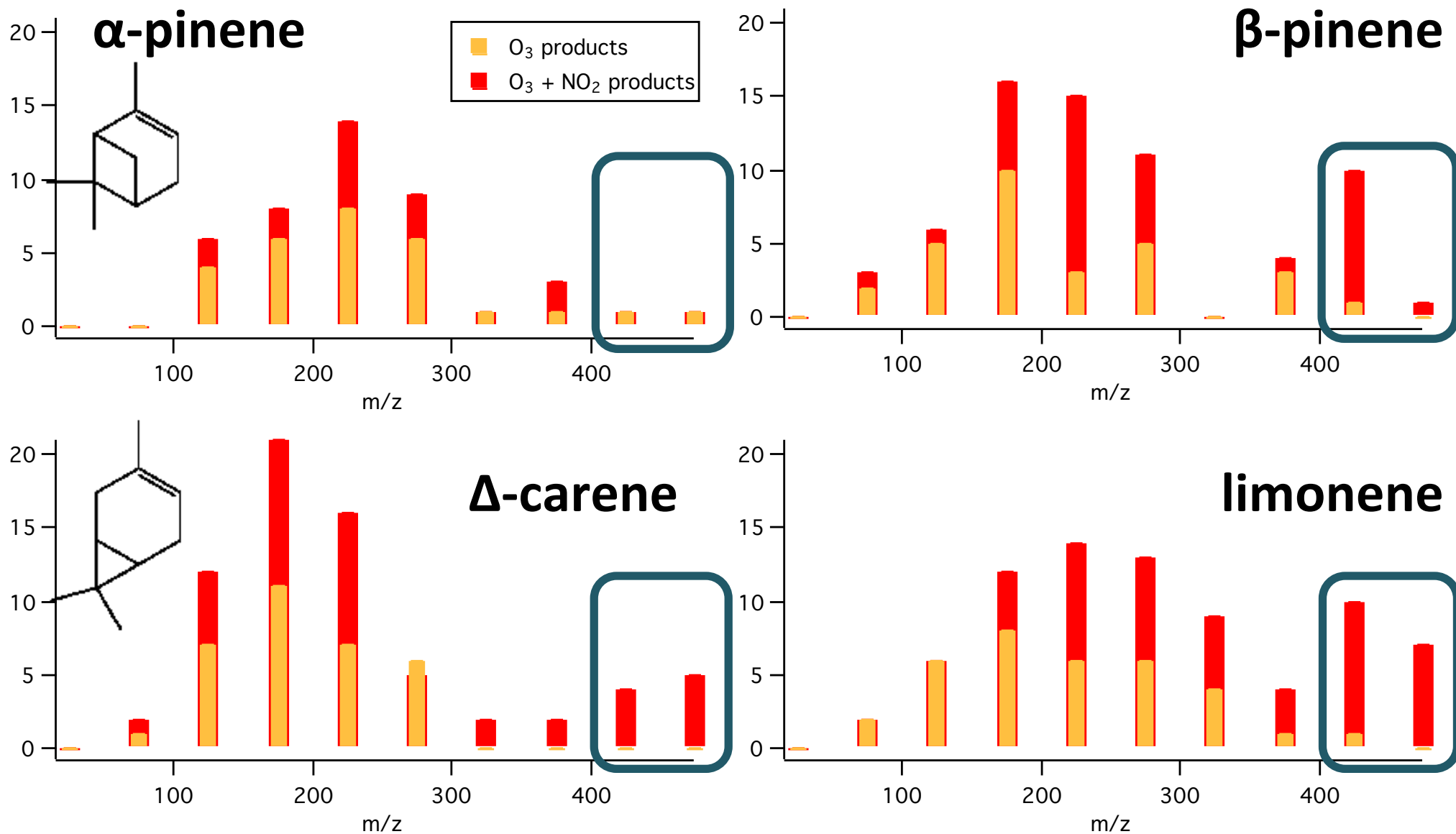
Observation #1a: SOA mass yield for O₃ + BVOC at varying [NO₂] is suppressed by NO₂ **only** for α-pinene



Danielle Draper ('13)



Observation #1b: Product mass distributions measured by offline HPLC-ESI-MS differ at high m/z

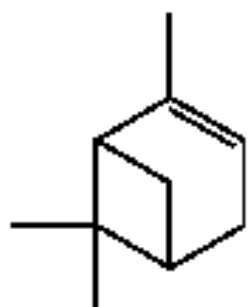


Draper et al., ACP 2015; collaboration with **Delphine Farmer** and **Yury Desyaterik** (CSU)

Observation #2: α -pinene vs. Δ -carene SOA yield difference is **NOT** affected by RO₂ reaction partner, inorganic seed

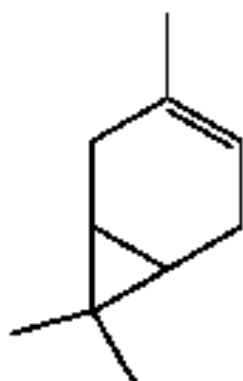


Hyungu Kang ('15)



α -pinene

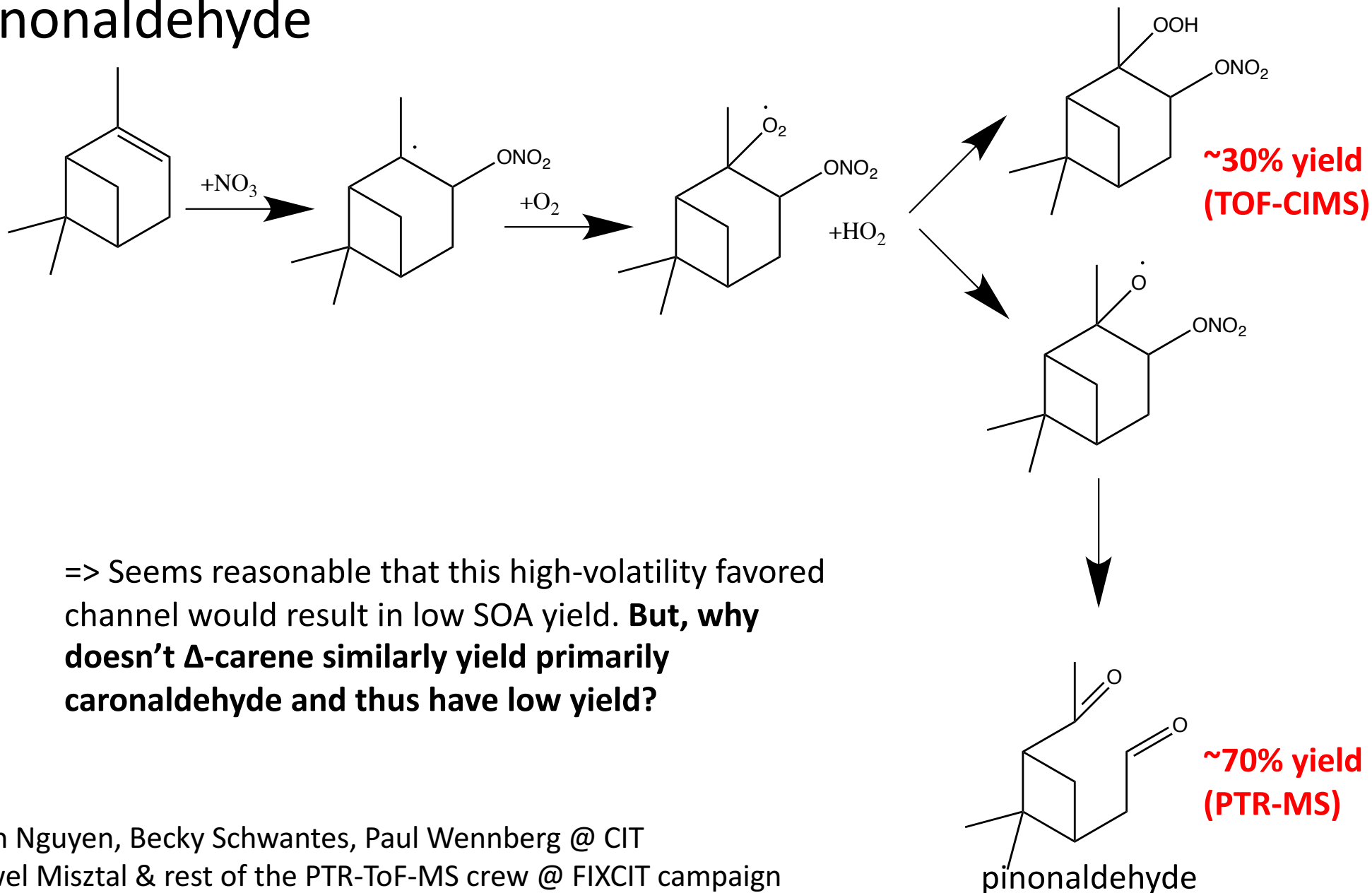
No.	Regime	SOA yield (AMS)	NO ₃ :Org
6	NO ₃ +RO ₂	3%	0.08
14	RO ₂ +RO ₂ , seeded	1%	0.10
17	HO ₂ +RO ₂	2%	0.17
<hr/>			
11c	RO ₂ +RO ₂	27%	0.09
13	NO ₃ +RO ₂	35%	0.15
16	HO ₂ +RO ₂ , seeded	37%	0.12
18c	RO ₂ +RO ₂ , seeded	40%	0.06
19	HO ₂ +RO ₂ , seeded	25%	0.14
22c	RO ₂ +RO ₂	104%	0.07
23	HO ₂ +RO ₂	21%	0.15



Δ -carene

Preliminary yield data, analysis in progress. Collaboration with **Jimenez group** at CU Boulder.
Kang et al., in preparation, 2018.

Observation #3: NO_3 + α -pinene under high $[\text{HO}_2]$ shows low yield of ROOH “termination” channel, high yield of pinonaldehyde

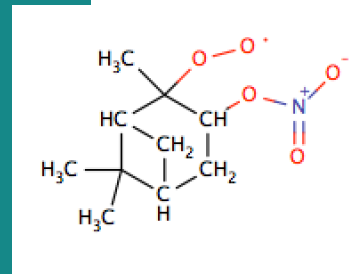
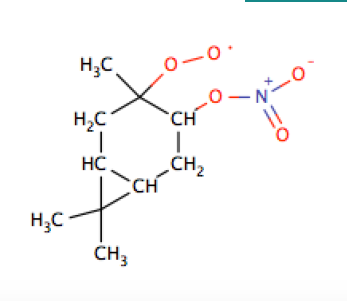
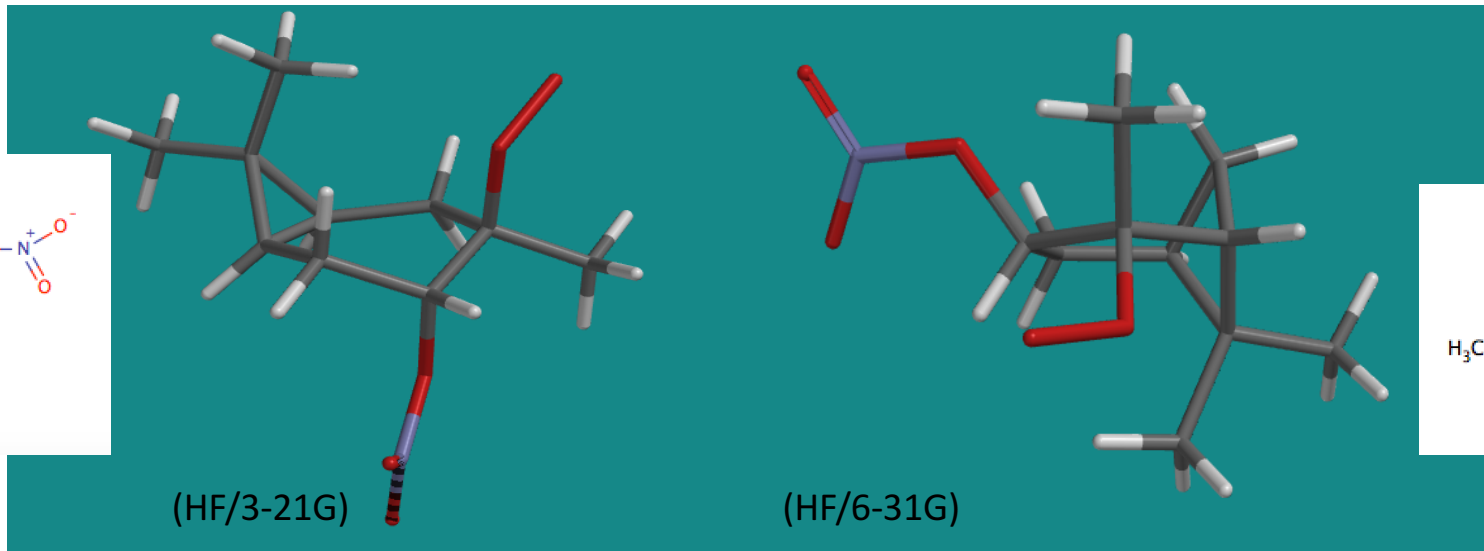


=> Seems reasonable that this high-volatility favored channel would result in low SOA yield. **But, why doesn't Δ -carene similarly yield primarily caronaldehyde and thus have low yield?**

First attempts to calculate nitrooxy-RO₂ structures using Spartan

Δ -carene

α -pinene



Cat Neshyba
(‘17)



Katie Stellmach
(‘18)



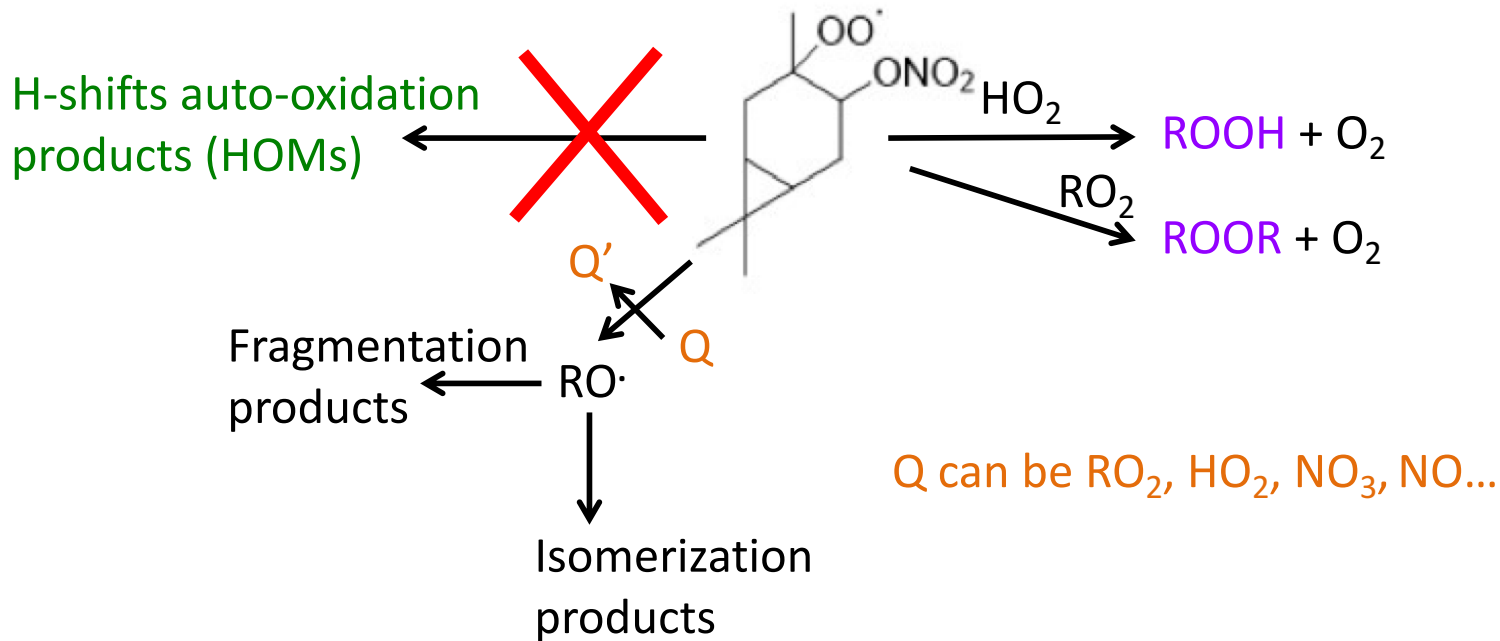
Hypothesis: Δ -carene nitrate-RO₂ can rapidly auto-oxidize to yield low-volatility products...



... while in α -pinene nitrate-RO₂, no H-abstraction is possible, because of structural constraints

Could this be the reason for α -pinene’s anomalous behavior?

Upping the computational game with the COPENHEL supergroup: Calculating reaction barriers for each RO₂'s options



Kristian Møller



Theo Kurtén

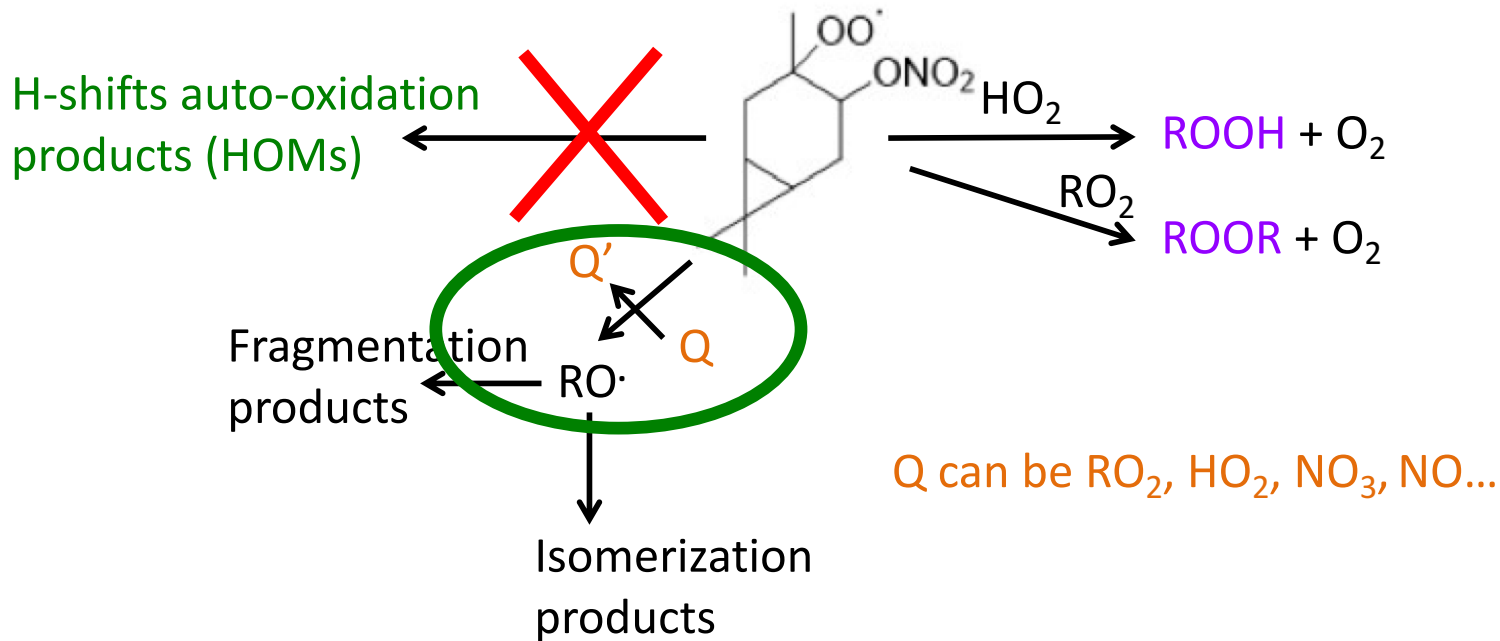


Henrik Kjaergaard

- The rates for all accessible H-shift reactions are below 10^{-4} s^{-1} for both monoterpenes.**

=> The peroxy radicals thus have lifetimes long enough to undergo bimolecular reactions, which occur on a timescale of ~ 0.01 and 100s

Upping the computational game with the COPENHEL supergroup: Calculating reaction barriers for each RO₂'s options



- The rates for all accessible H-shift reactions are below 10⁻⁴ s⁻¹ for both monoterpenes.**
- However, the alkoxy-forming pathway is thermodynamically accessible for both monoterpenes.**

=> What is the fate of these nitrooxy-alkoxy radicals (RO·) from α-pinene and Δ-carene?



Kristian Møller



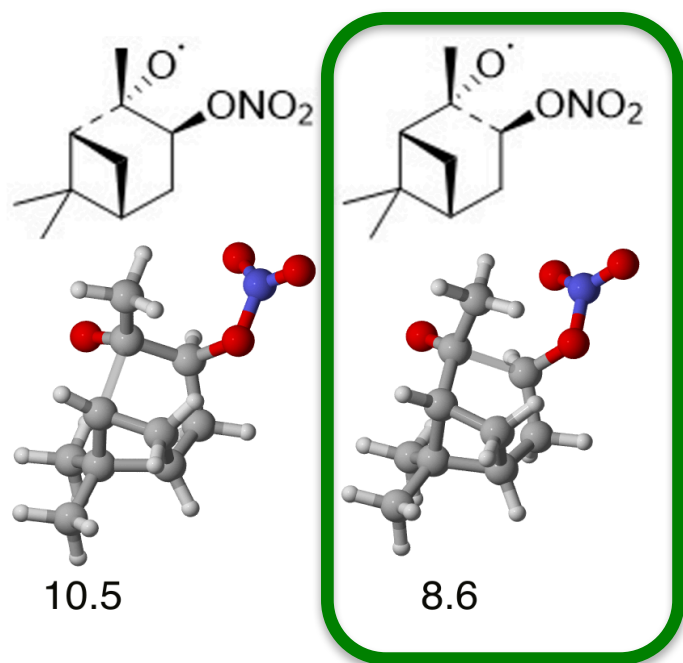
Theo Kúrten



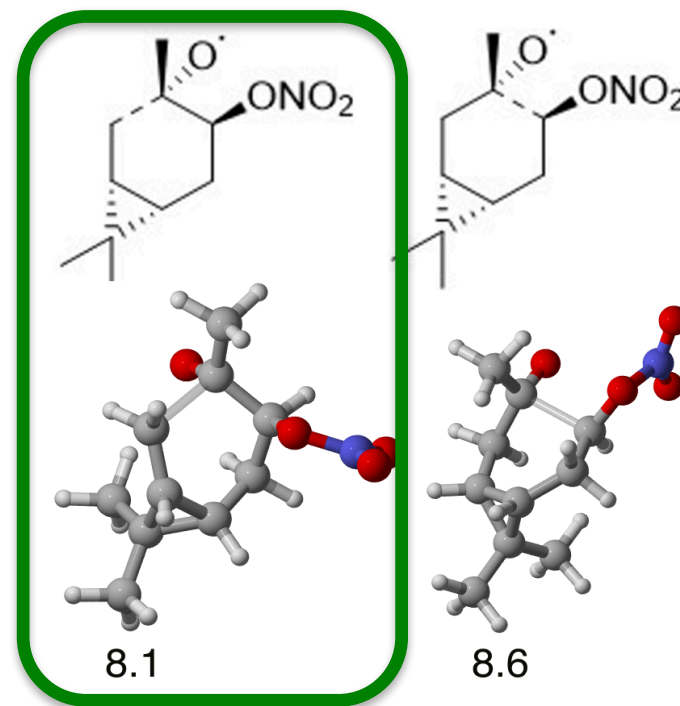
Henrik Kjaergaard

Calculated bond scission reaction barriers for alkoxy radicals

α -pinene



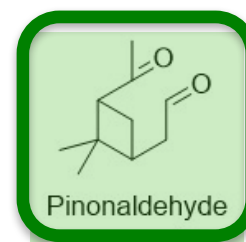
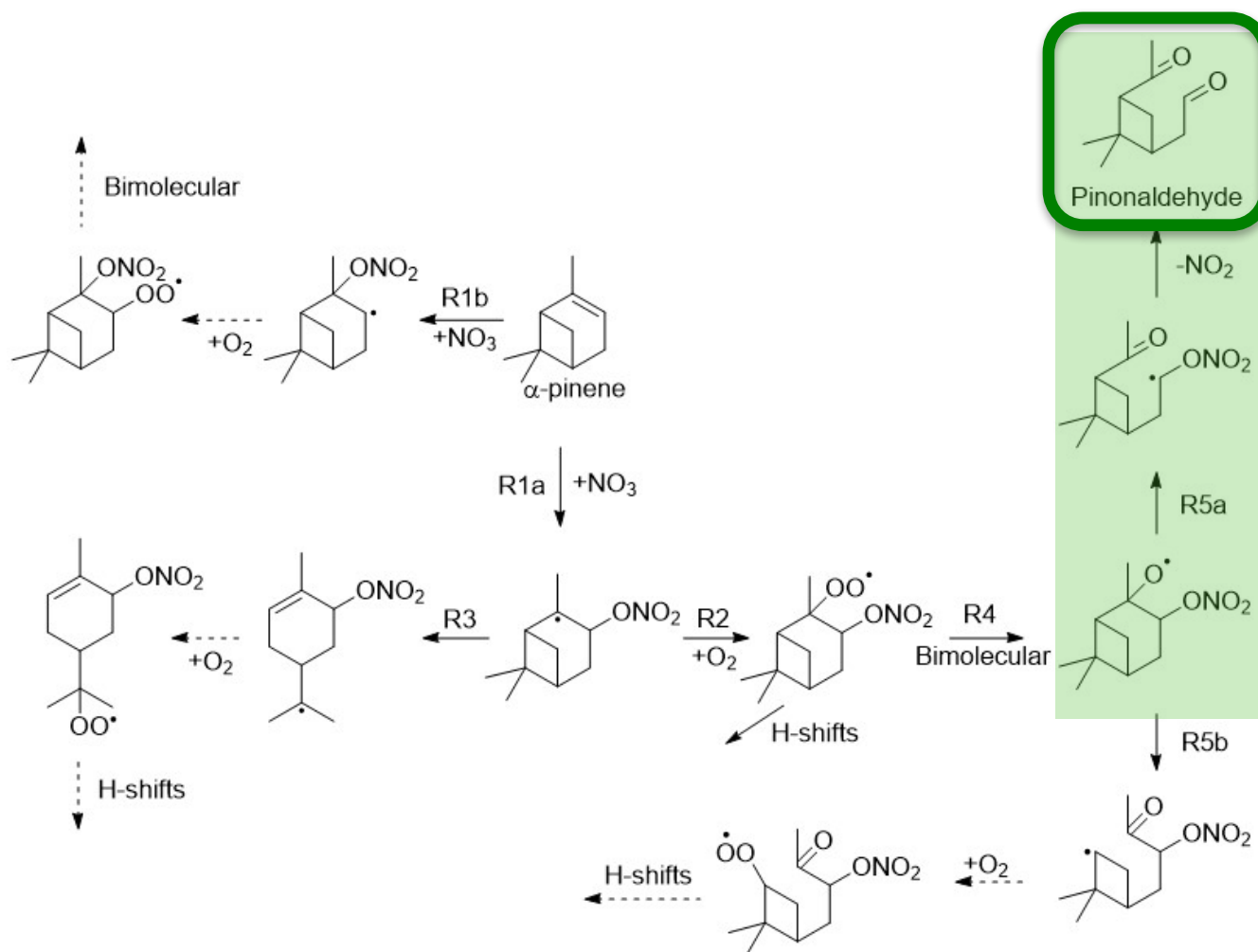
Δ -carene



Bond scission transition states

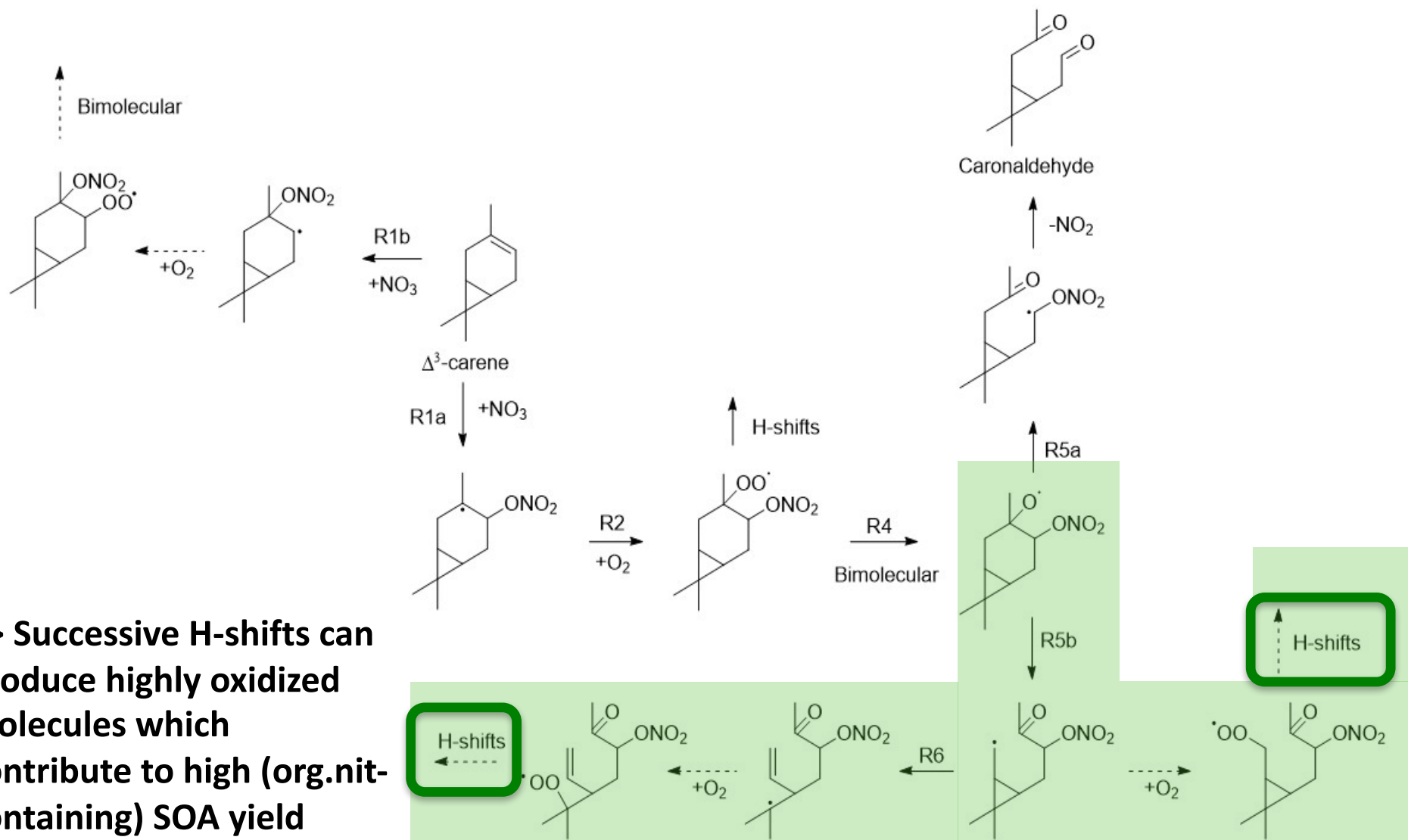
Calculated reaction barriers in kcal mol⁻¹ (zero-point corrected ω B97X-D/aug-cc-pVTZ electronic energy differences between the lowest-energy transition states and reactants)

Based on these different bond scission pathways, α -pinene will produce primarily pinonaldehyde...



**Volatile =>
low SOA yield**

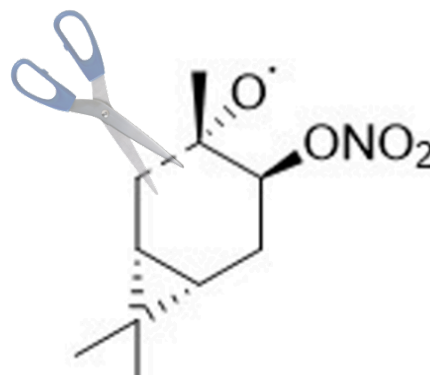
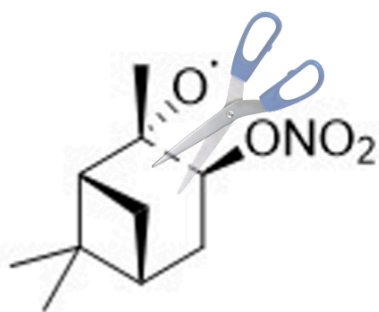
...while most Δ -carene will retain the nitrate group and may go on to later-generation H-shifts



=> Successive H-shifts can produce highly oxidized molecules which contribute to high (org.nit-containing) SOA yield

Conclusions on molecular structure and NO_3 + monoterpene SOA

- Different preferred alkoxy scission pathways may explain huge SOA yield difference between α -pinene and Δ -carene

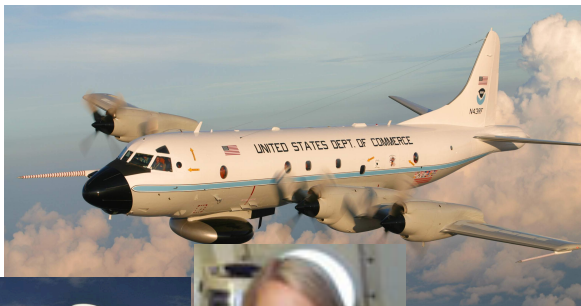


- Unfortunately, this means one can't really lump monoterpenes in SOA mechanisms

Thank you:

- Collaborators for the NO_3 + isoprene analysis @ NOAA ESRL Chemical Sciences Division & CU Boulder
- Collaborators for the NO_3 + α -pinene vs. Δ -carene calculations @ Uni Copenhagen and Uni Helsinki
- JLF Funding:
NOAA AC4 #NA13OAR4310070; EPA STAR Program #RD-83539901
Fulbright U.S. Scholar grant in the Netherlands

Want to talk more?
Julie Fry: fry@reed.edu



Steve
Brown



Pete
Edwards



Ann
Middlebrook



Jose
Jimenez



Doug
Day



Theo
Kúrten



Paul
Wennberg

Henrik
Kjaergaard

Kristian
Møller