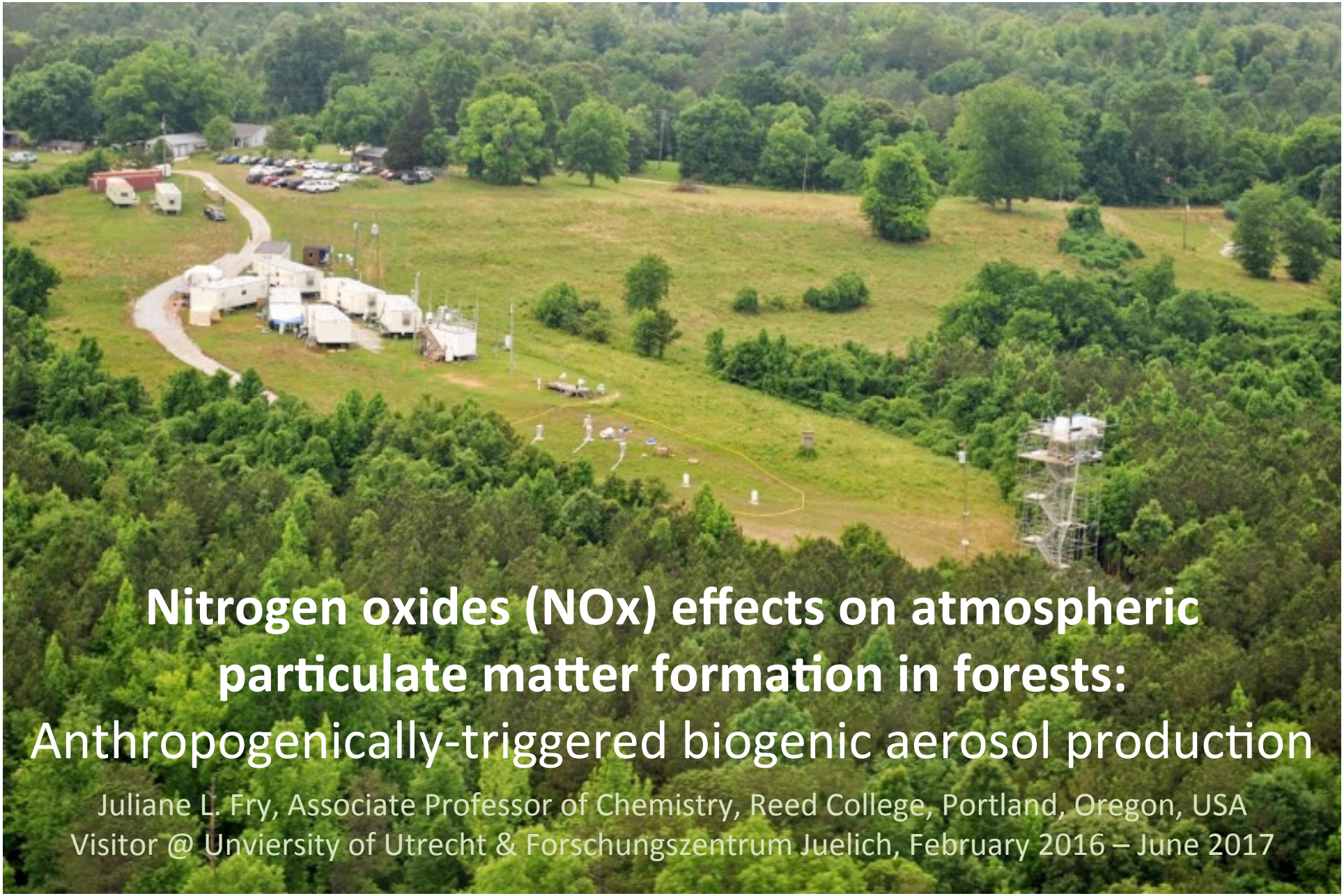
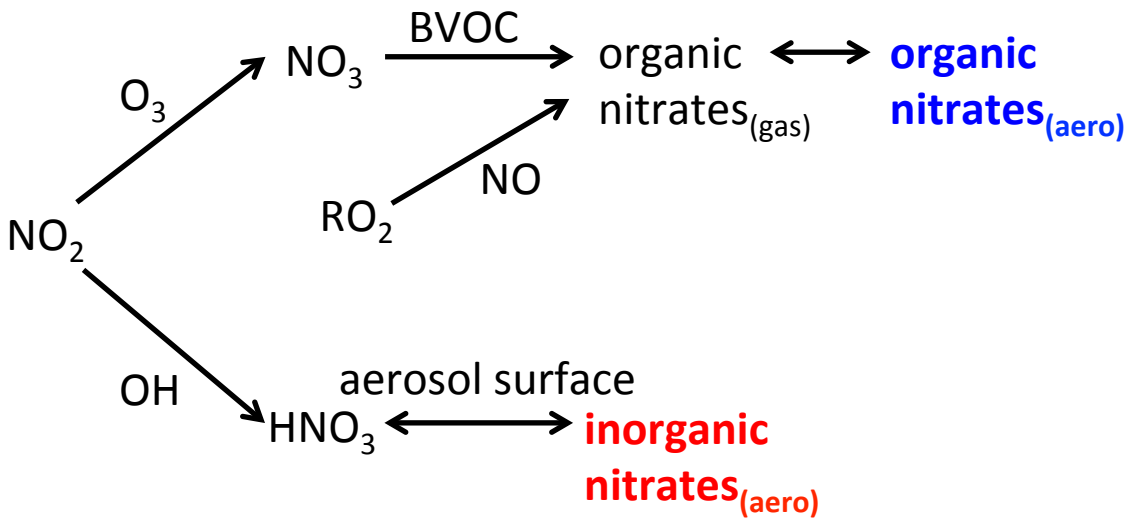


Nitrogen oxides (NOx) effects on atmospheric particulate matter formation in forests: Anthropogenically-triggered biogenic aerosol production

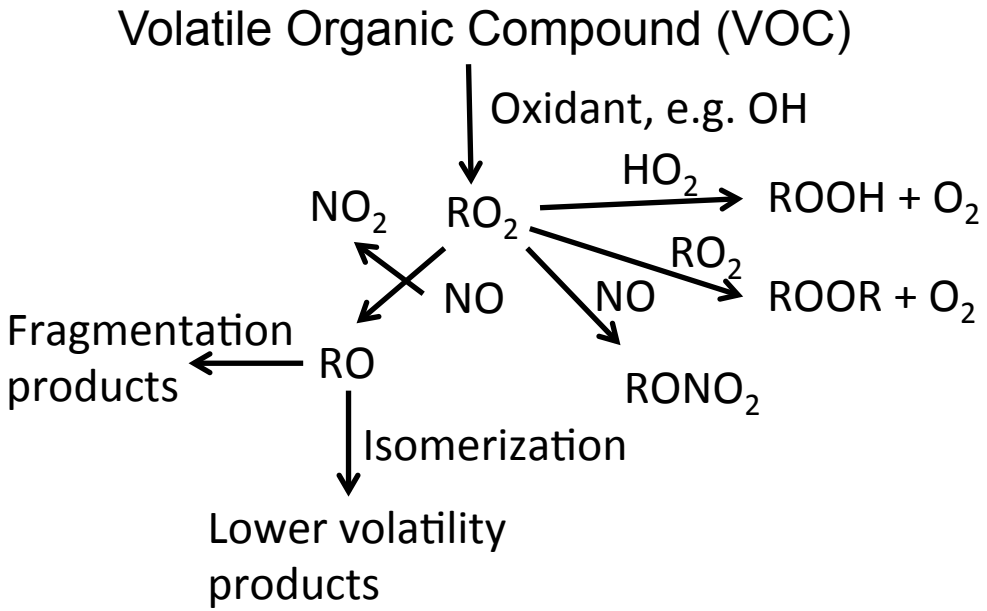
Juliane L. Fry, Associate Professor of Chemistry, Reed College, Portland, Oregon, USA
Visitor @ Unviersity of Utrecht & Forschungszentrum Juelich, February 2016 – June 2017

Our piece of the puzzle: determining NOx fate

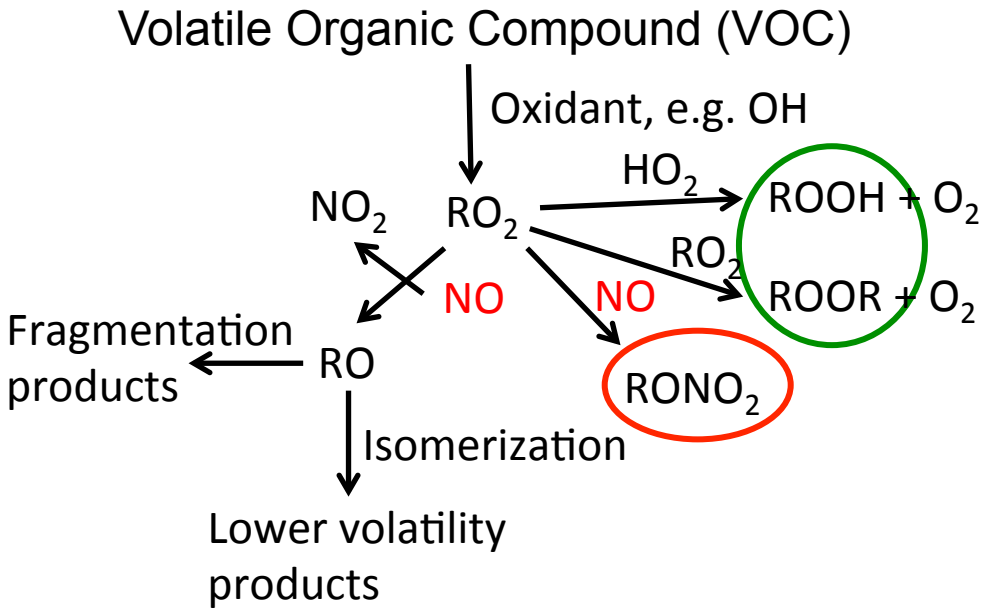


=> Measure organonitrate and inorganic nitrate gas/aerosol partitioning

SOA Chemistry 101: What are the possible effects of NO_x on SOA formation?

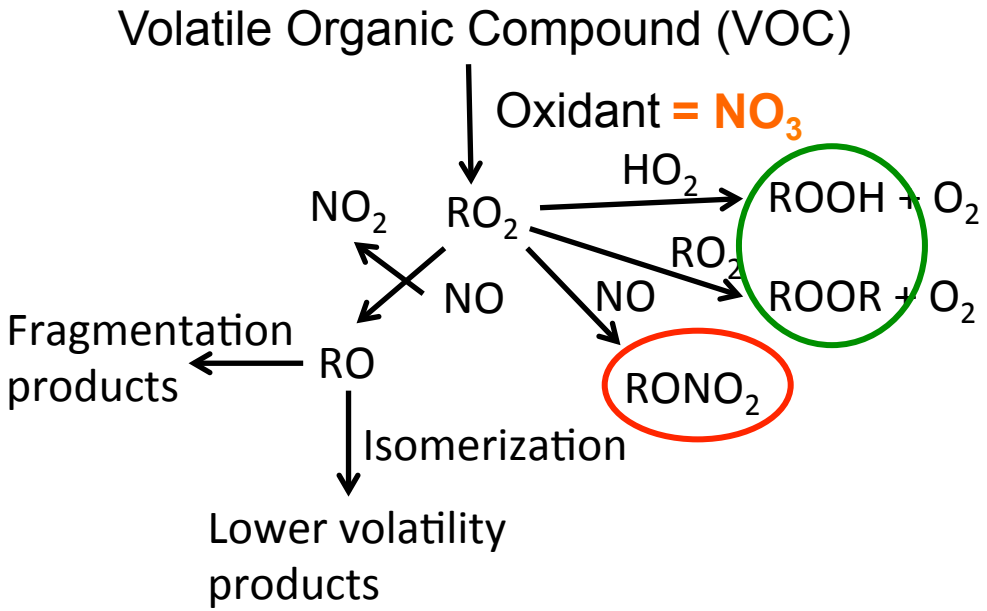


SOA Chemistry 101: What are the possible effects of NO_x on SOA formation?



1) [NO] controls fate of RO_2 radical: can enhance or suppress SOA depending on relative volatilities of products

SOA Chemistry 101: What are the possible effects of NO_x on SOA formation?

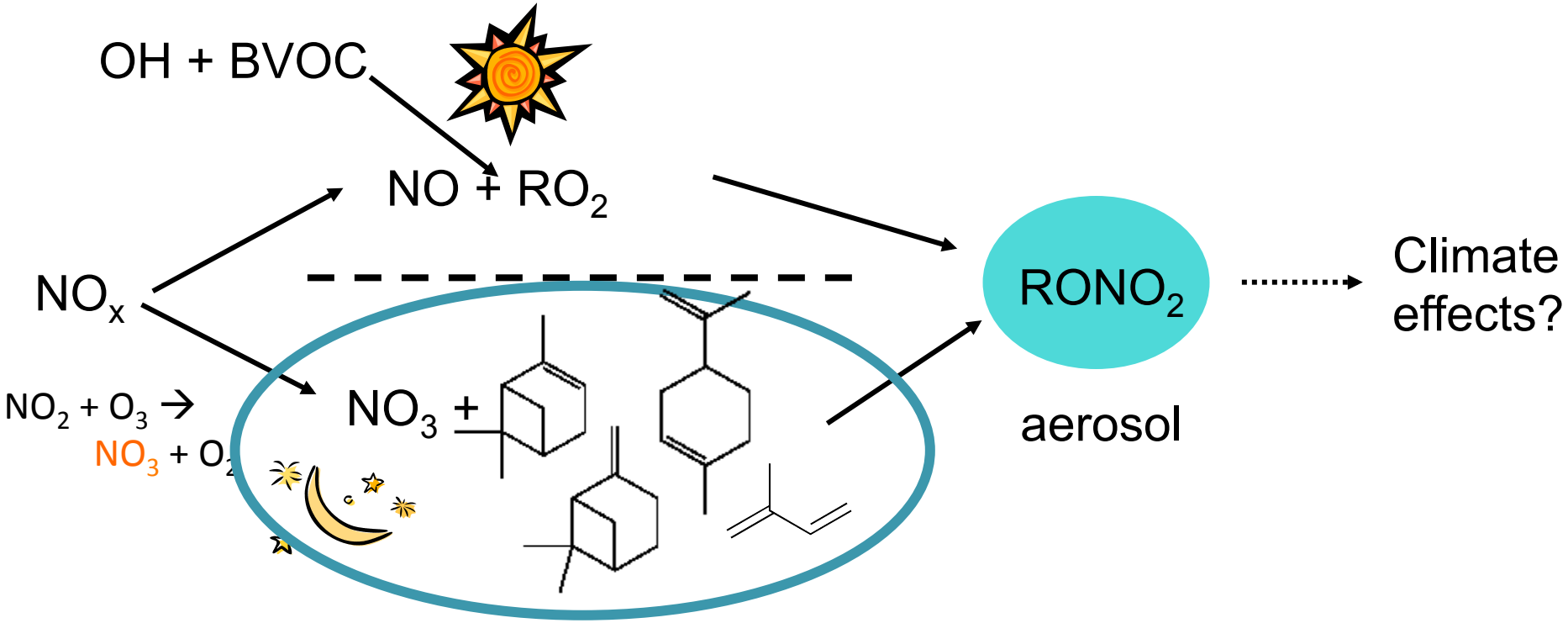


$NO_2 + O_3 \rightarrow$ **NO_3** $+ O_2$
mostly nighttime because NO_3 photolyzes rapidly

1) [NO] controls fate of RO_2 radical: can enhance or suppress SOA depending on relative volatilities of products

2) Adds an **additional mechanism** of aerosol formation: NO_3 + BVOC

What is the role of NO_x in oxidative SOA formation? Net suppression or enhancement?



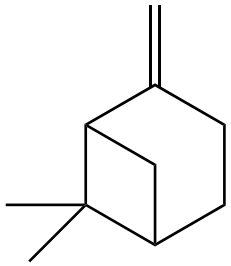
=> Do these day (OH ox) & night (NO_3 ox) mechanisms make two distinct classes of nitrates, with different consequences for SOA formation?

=> Could this relatively less well-studied but rapid NO_3-initiated chemistry play an important role in new particle growth, especially in high-BVOC plumes?

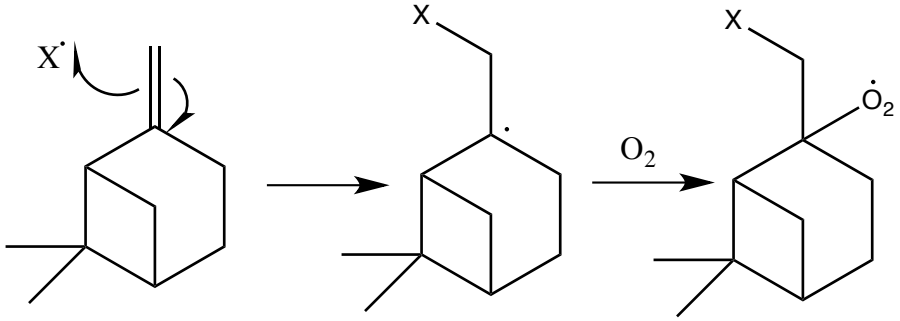
=> How does this chemistry compete with other fates of NOx?

SOA Chemistry 201: What are the effects of different oxidants on product structures?

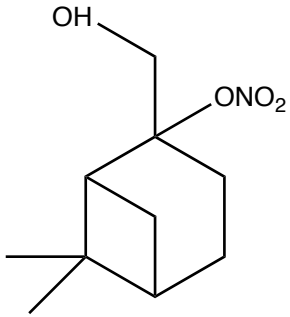
Representative BVOC: β-pinene:



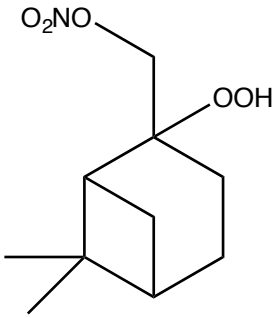
Radical ($X^{\cdot}$) reaction proceeds via attack on double bond, to yield the most substituted carbon radical, which rapidly picks up O_2 and becomes a peroxy radical ("RO_2"):



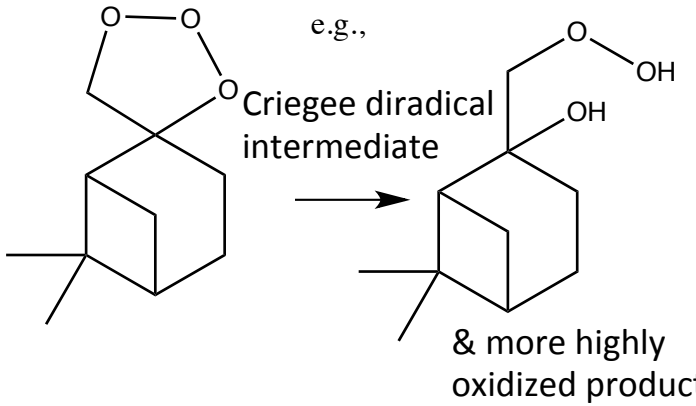
So, OH radicals make more of <u>these</u> nitrates:



While NO_3 radicals make more of <u>these</u> nitrates:



And O_3 isn't a radical and makes more of a mess:



Some mechanism papers: Winterhalter et al., O_3 + bpin, J. Atm. Chem. 2000; Pinho et al., OH + bpin, J. Atm. Chem. 2007; Fry et al., NO_3 + bpin, ACP 2009

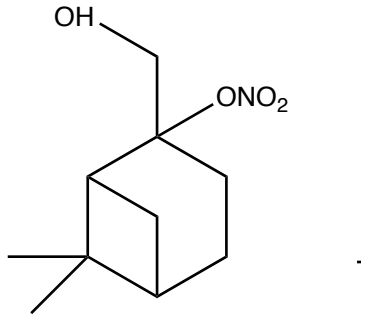
SOA Chemistry 201: What are the effects of different oxidants on product structures?

Who cares??

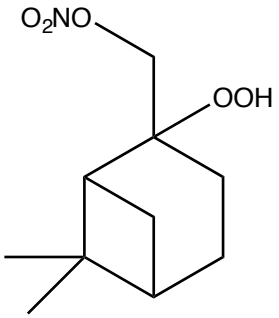
At atmospherically relevant humidity & pH, tertiary nitrates hydrolyze rapidly to HNO_3!

Rindelaub, et al., Atm. Env. 2014;
Hu et al., ACP 2011: **τ < 1 hr!**

So, OH radicals make more of these nitrates:



While NO_3 radicals make more of these nitrates:

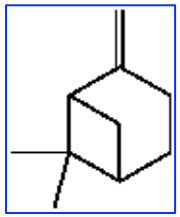


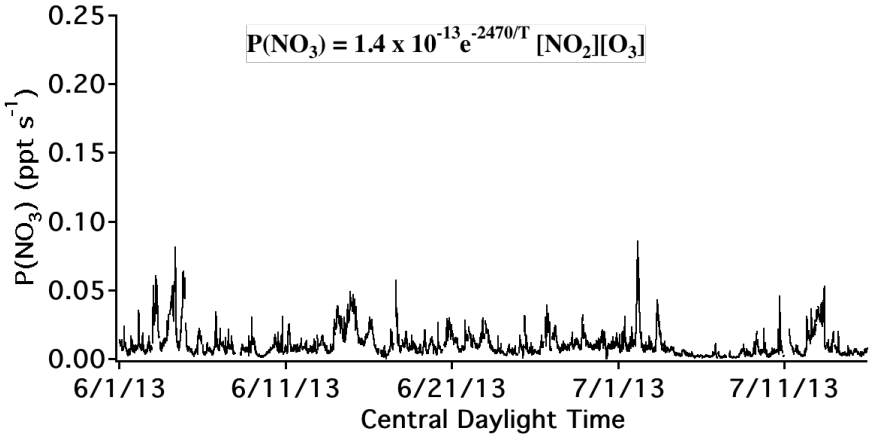
Primary/secondary nitrates hang around ~ forever (longer than particle lifetime)

Darer et al., ES&T 2011,
Hu et al., ACP 2011

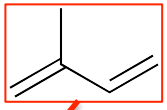
Some mechanism papers: Winterhalter et al., O_3 + bpin, J. Atm. Chem. 2000; Pinho et al., OH + bpin, J. Atm. Chem. 2007; Fry et al., NO_3 + bpin, ACP 2009

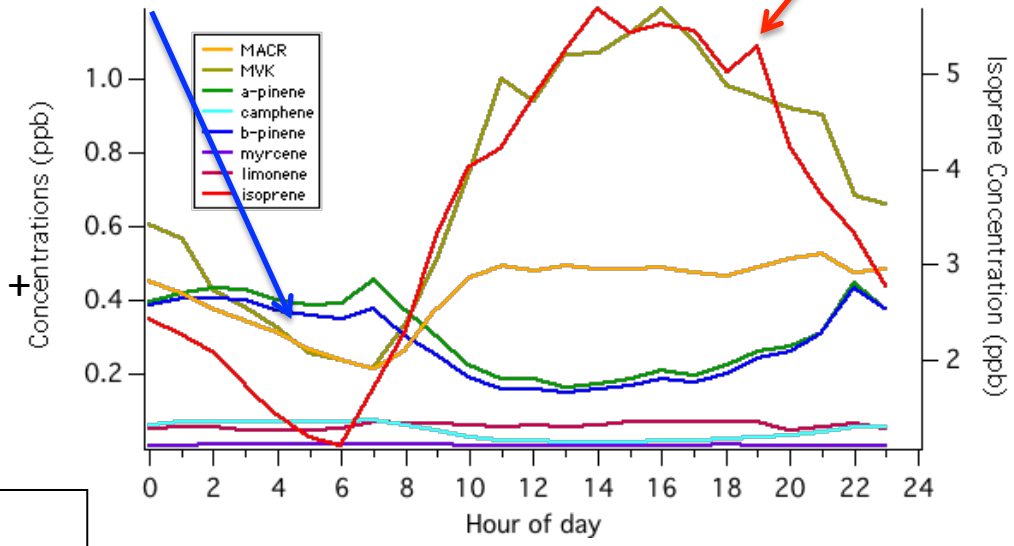
NO_3 + BVOC → organoNO_3 SOA

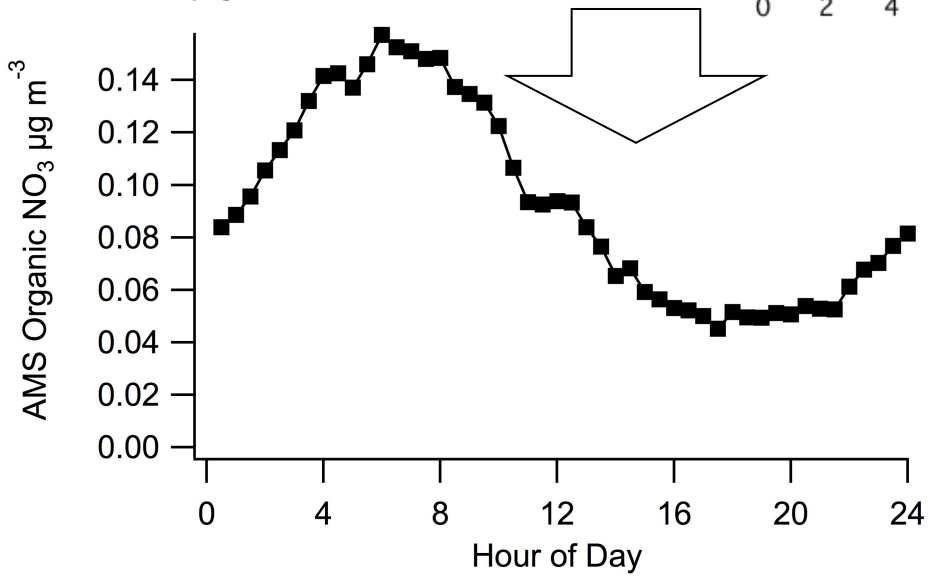




which BVOCs?

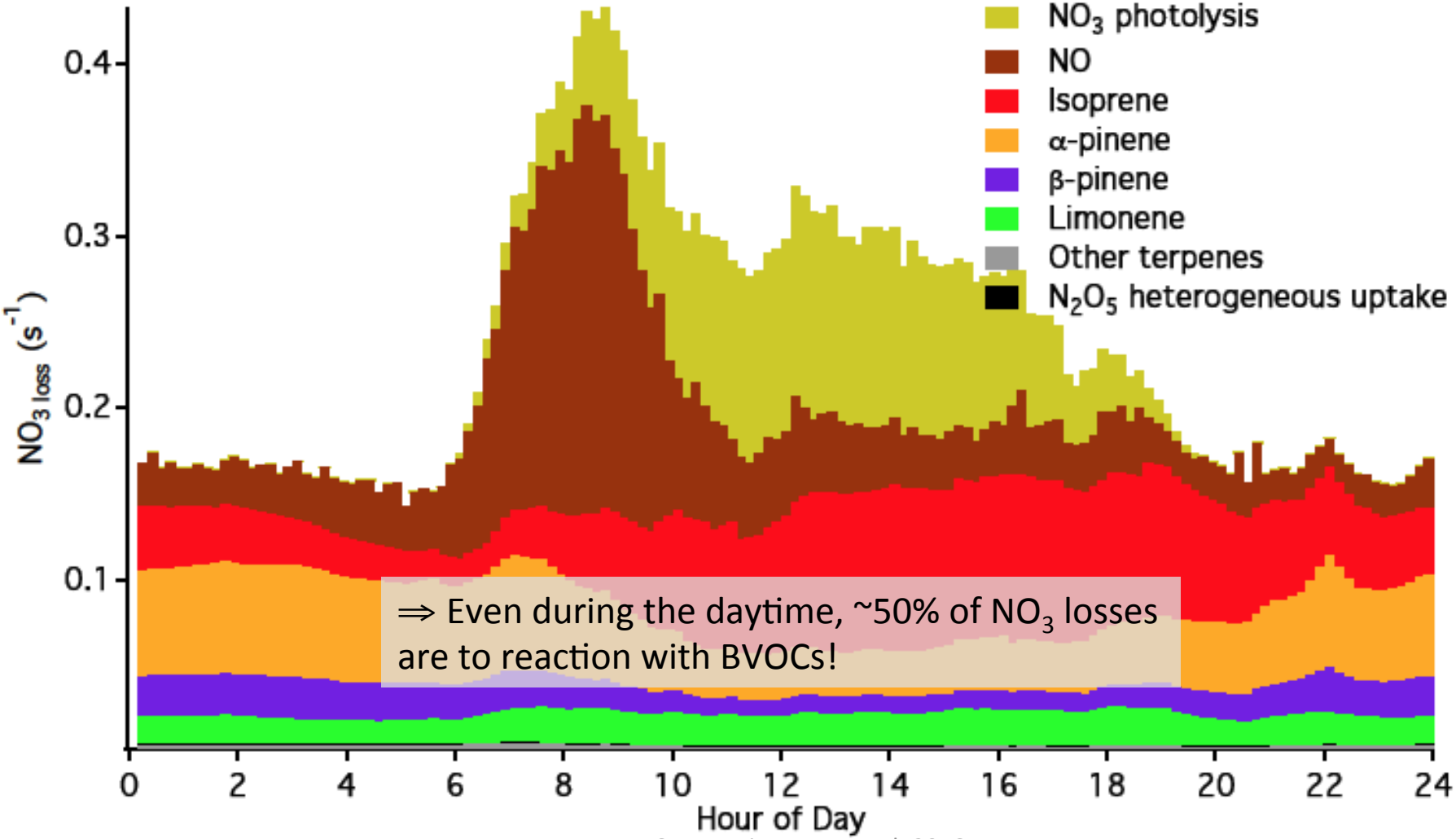






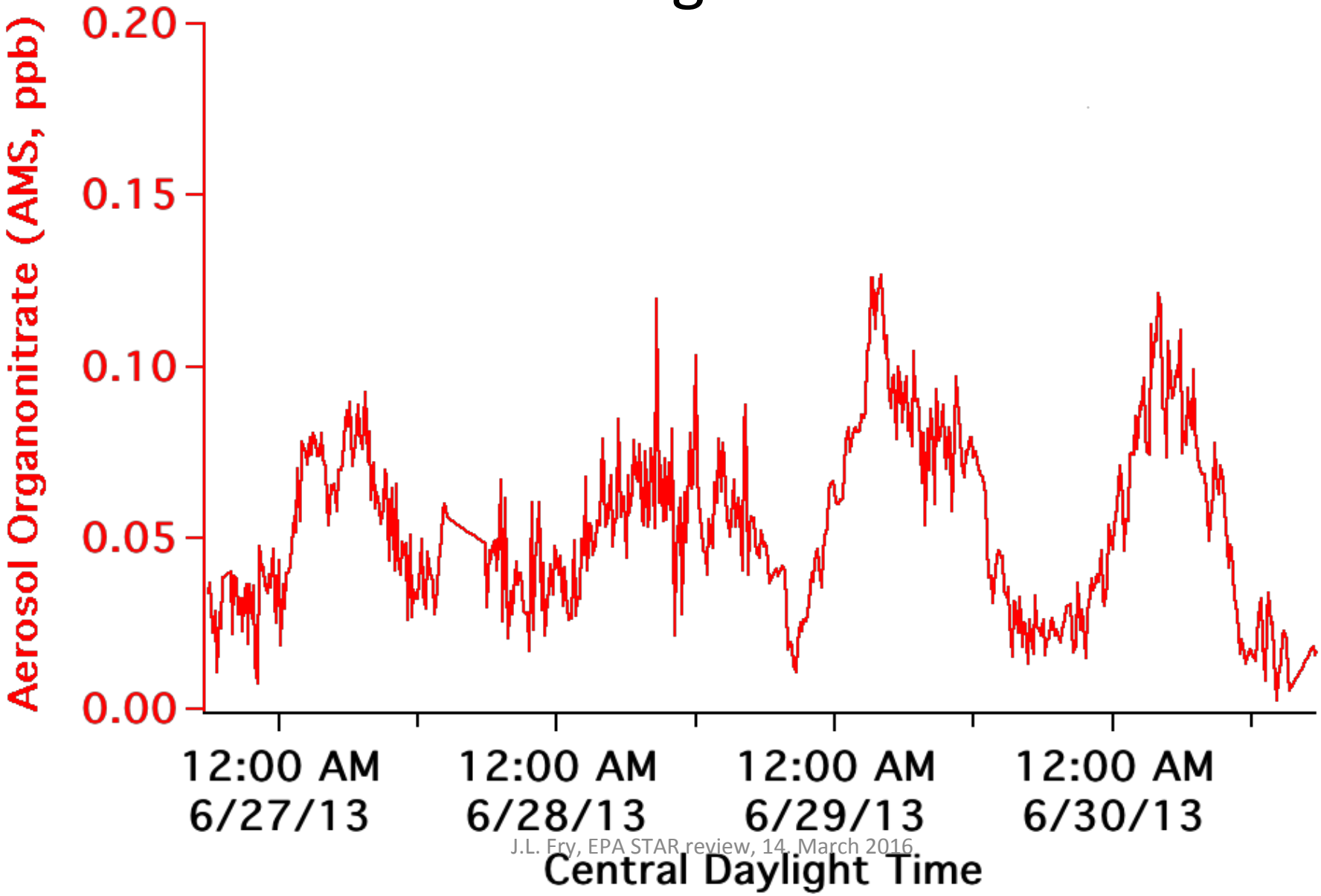
=> How much of NO_3 loss goes to reaction with BVOC over the diurnal cycle?

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



Ayres et al., ACP 2015

Demonstrating that NO_3+BVOC produces substantial organonitrate SOA



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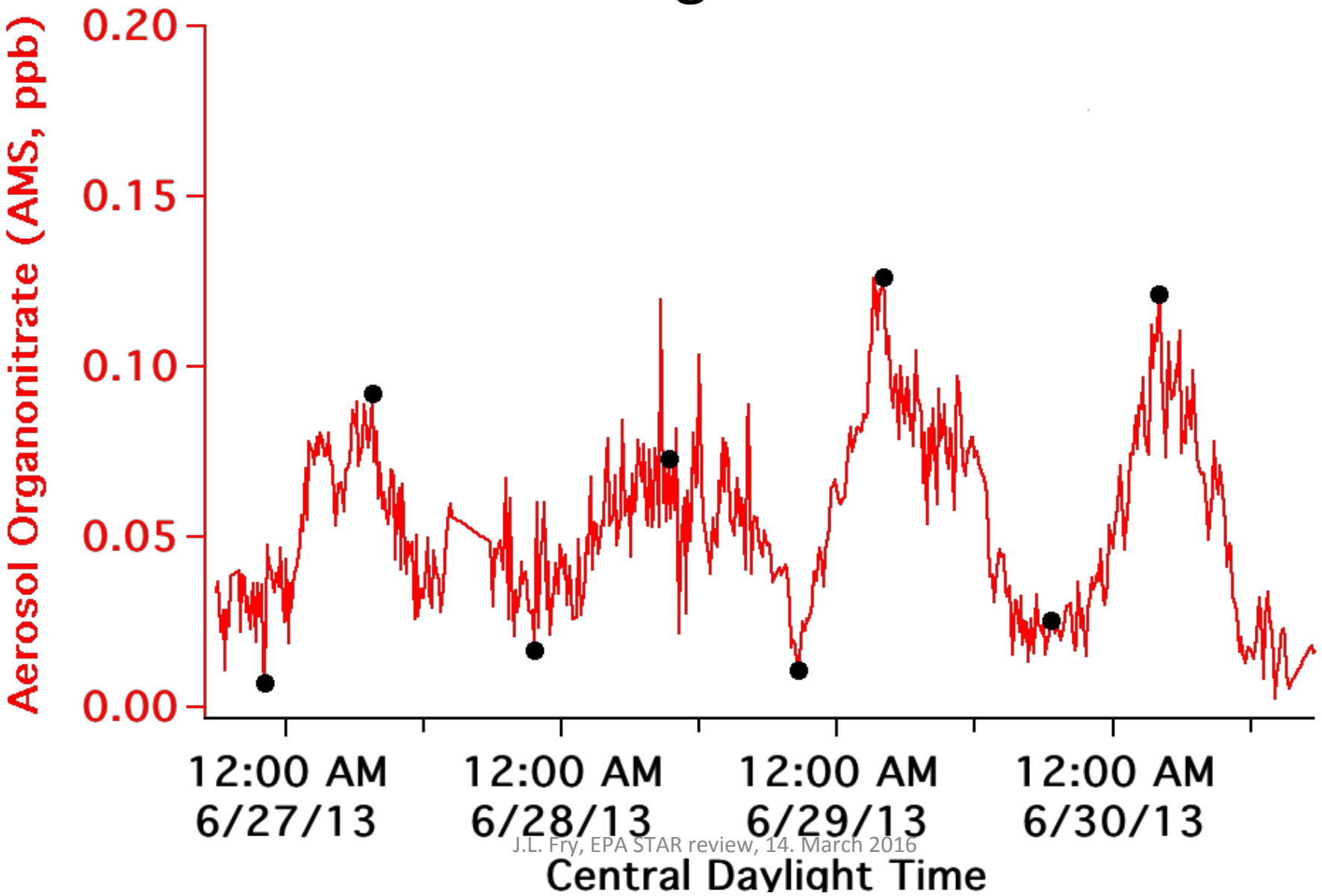

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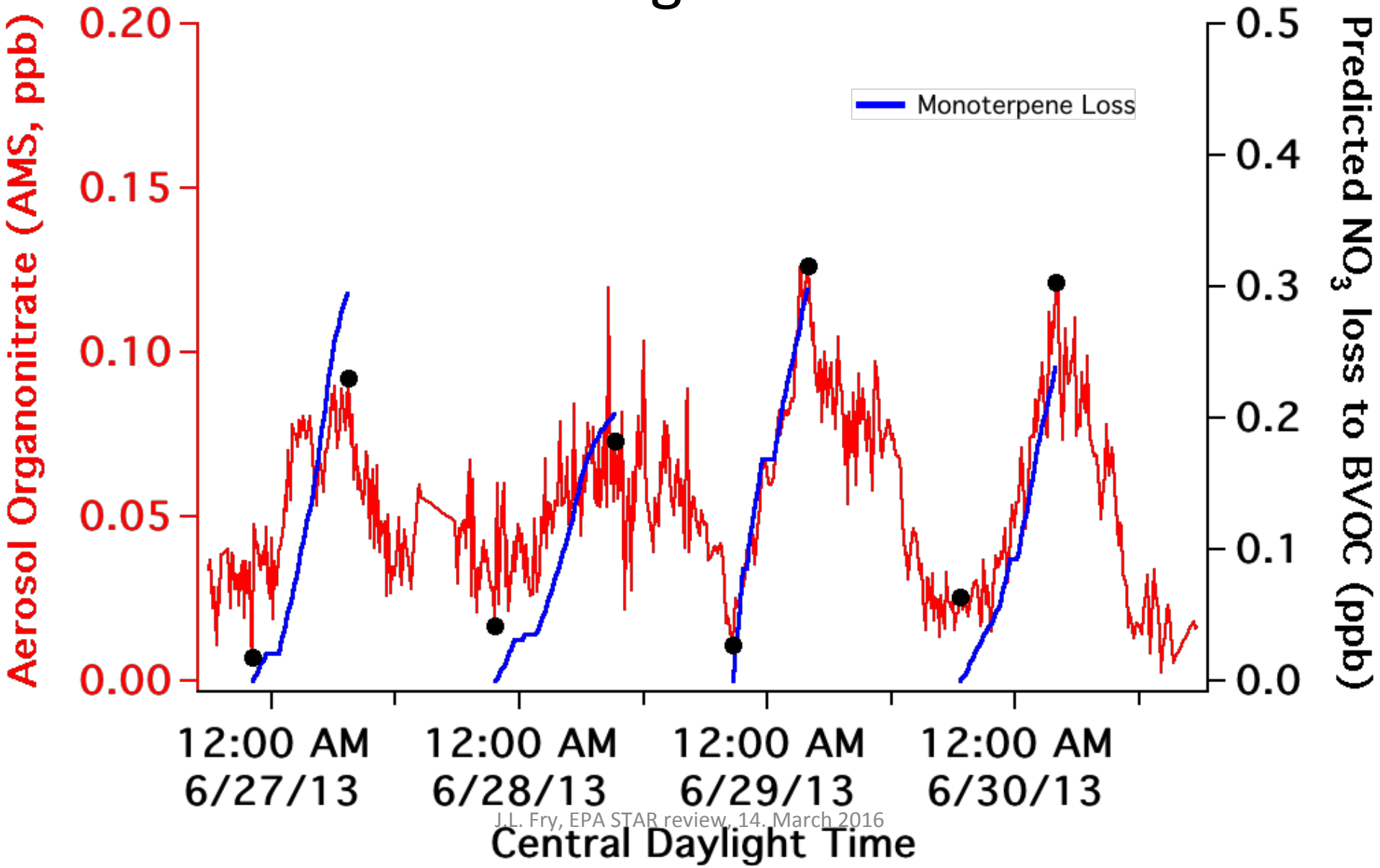
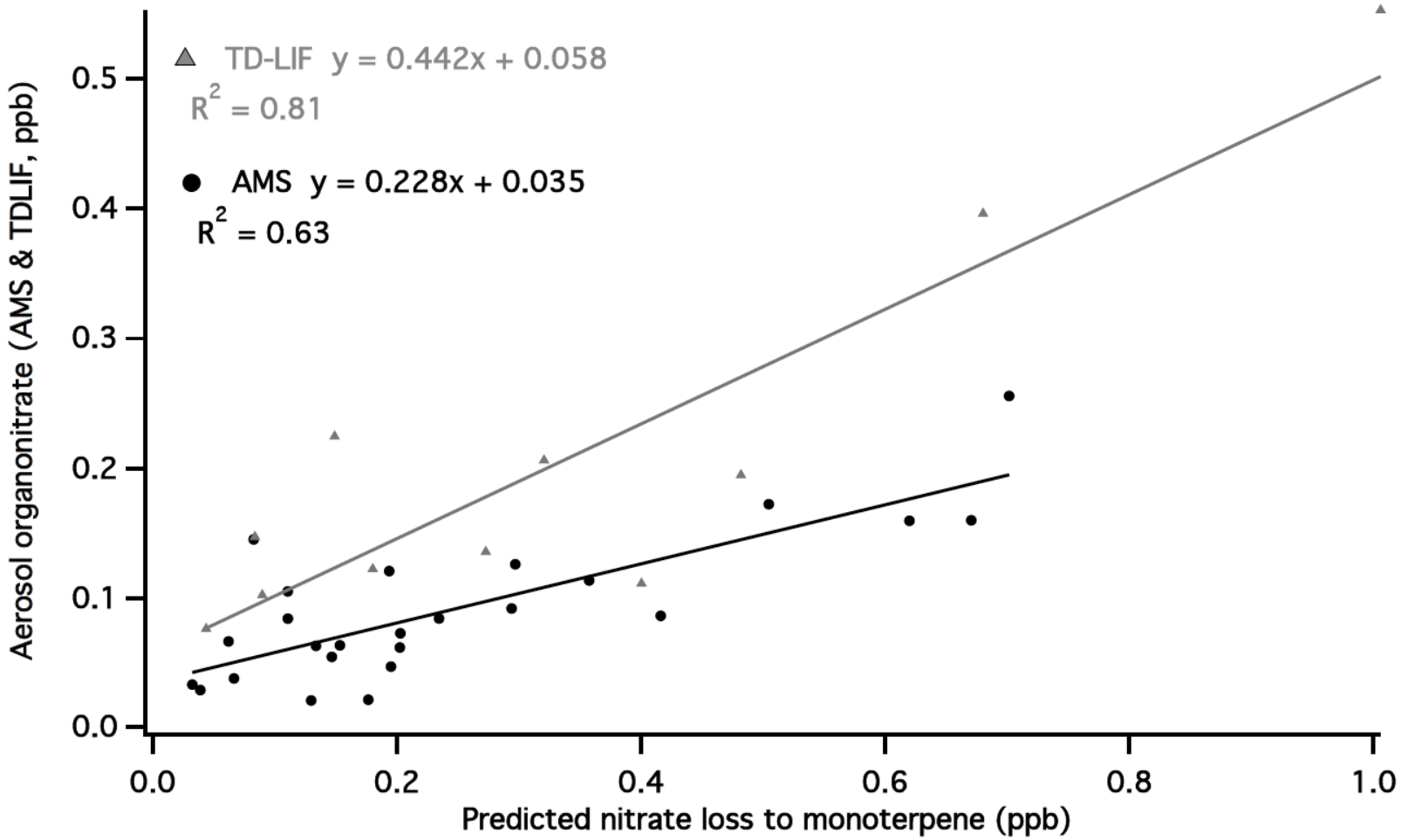


Aggregate molar organonitrate$_{aero}$ yield ~ 23-44 %

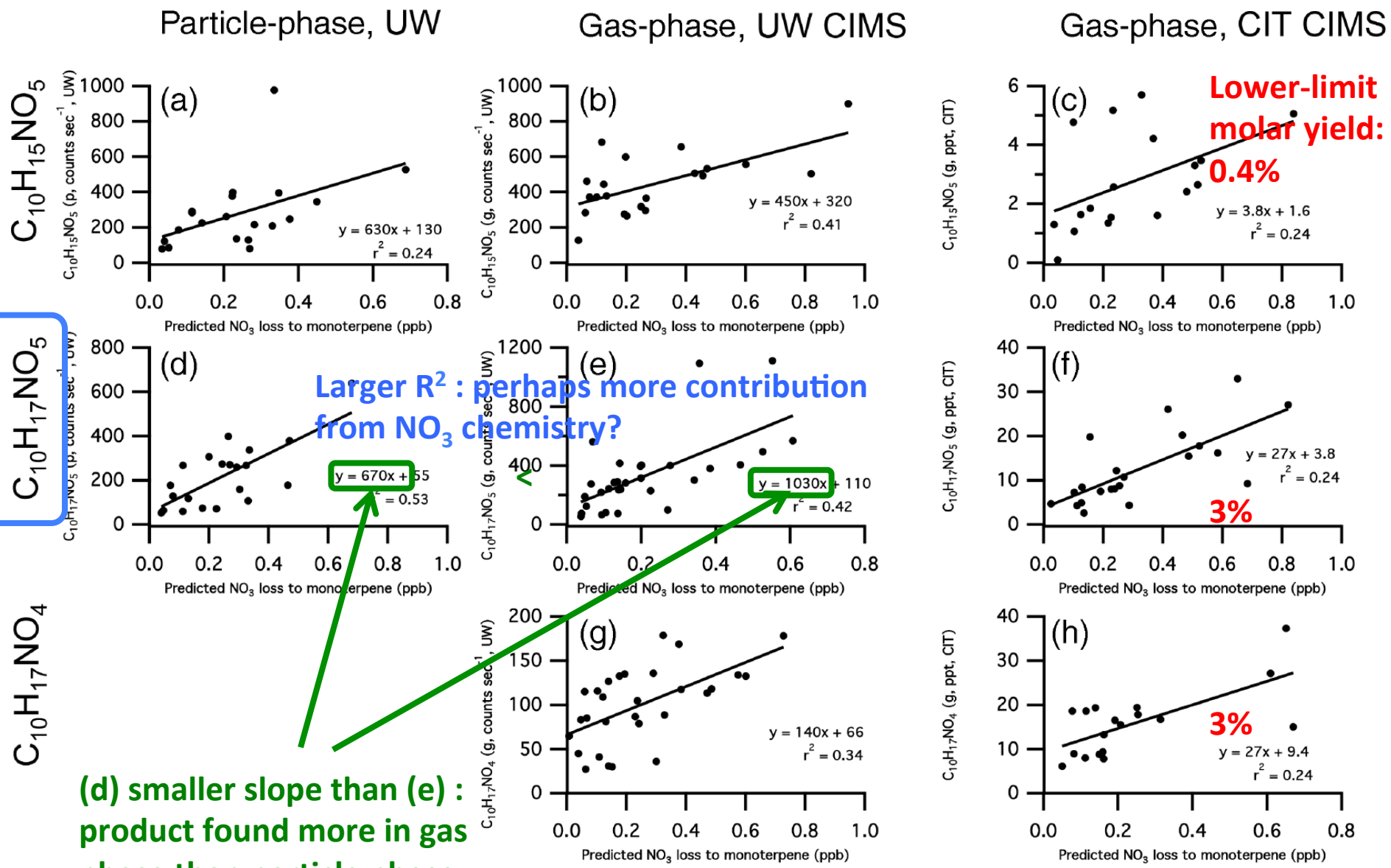
This molar yield translates to 42-81% aggregate mass yield (assumes MW=250 g mol^{-1})

Note: SOA mass yields from NO_3 + different BVOCs vary widely!



Ayres et al., ACP 2015.

Which organonitrates partition to the particle phase?



Lower-limit molar yield: 0.4%

3%

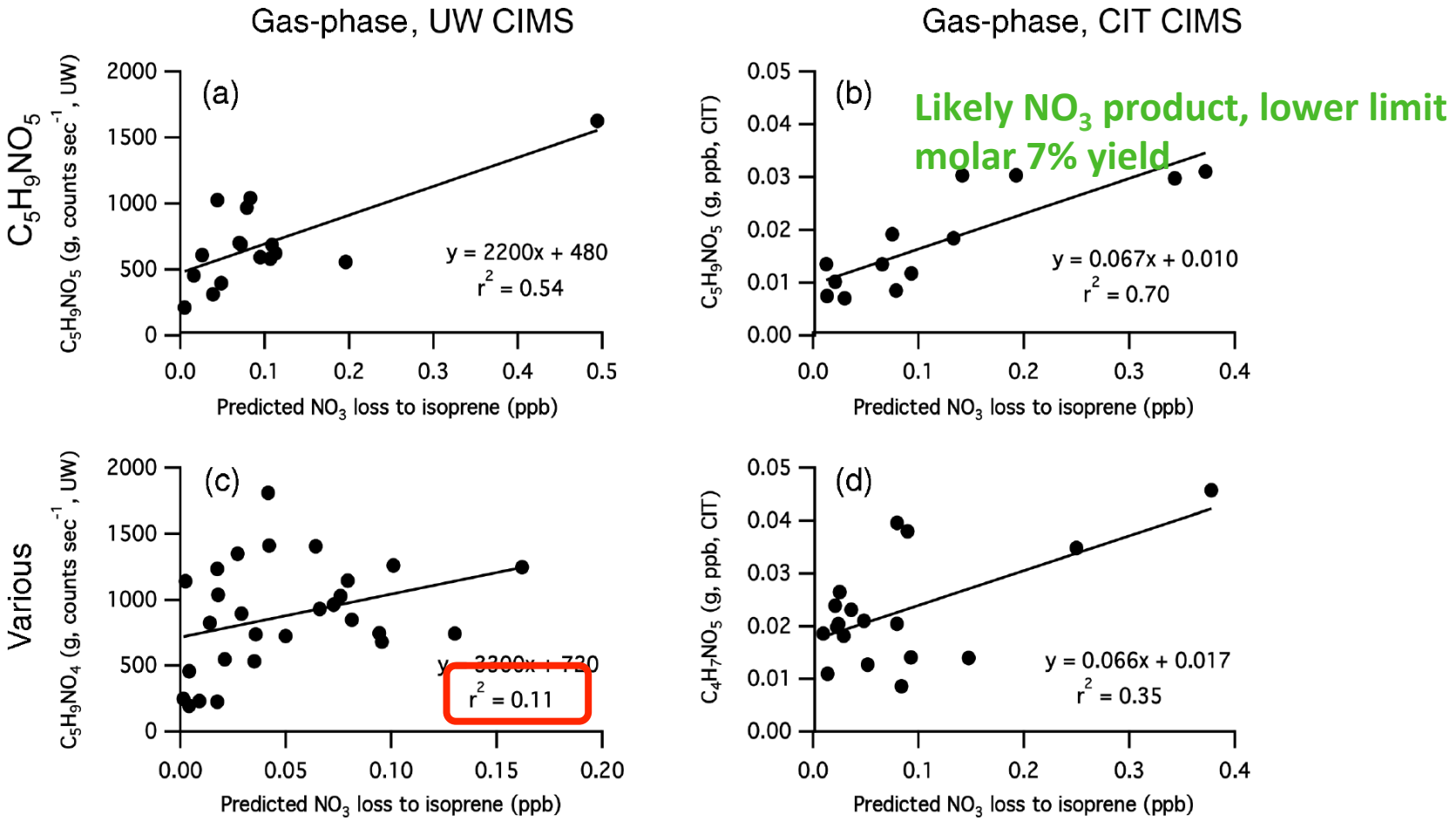
3%

Larger R^2 : perhaps more contribution from NO_3 chemistry?

(d) smaller slope than (e) : product found more in gas phase than particle phase

Ayres et al., ACP 2015.

Which organonitrates stay in the gas phase?
C_5 (likely isoprene-derived) organonitrates detected

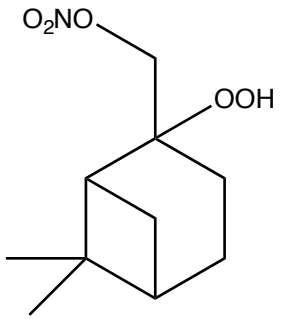


Ayres et al., ACP 2015.

Possible chemical structures of formulae observed, from β-pinene and isoprene oxidation:

More NO_3 source contrib:

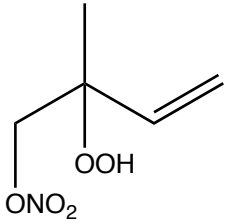
$C_{10}H_{17}NO_5$



Obs. in aerosol-phase:

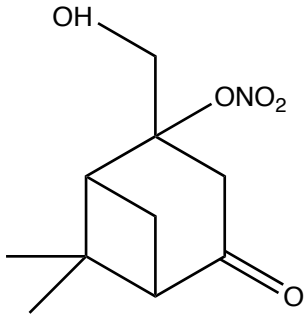
$C_5H_9NO_5$

Obs. in gas-phase:

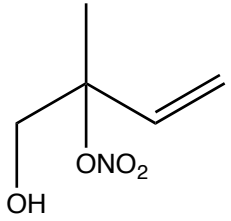


Less:

$C_{10}H_{15}NO_5$



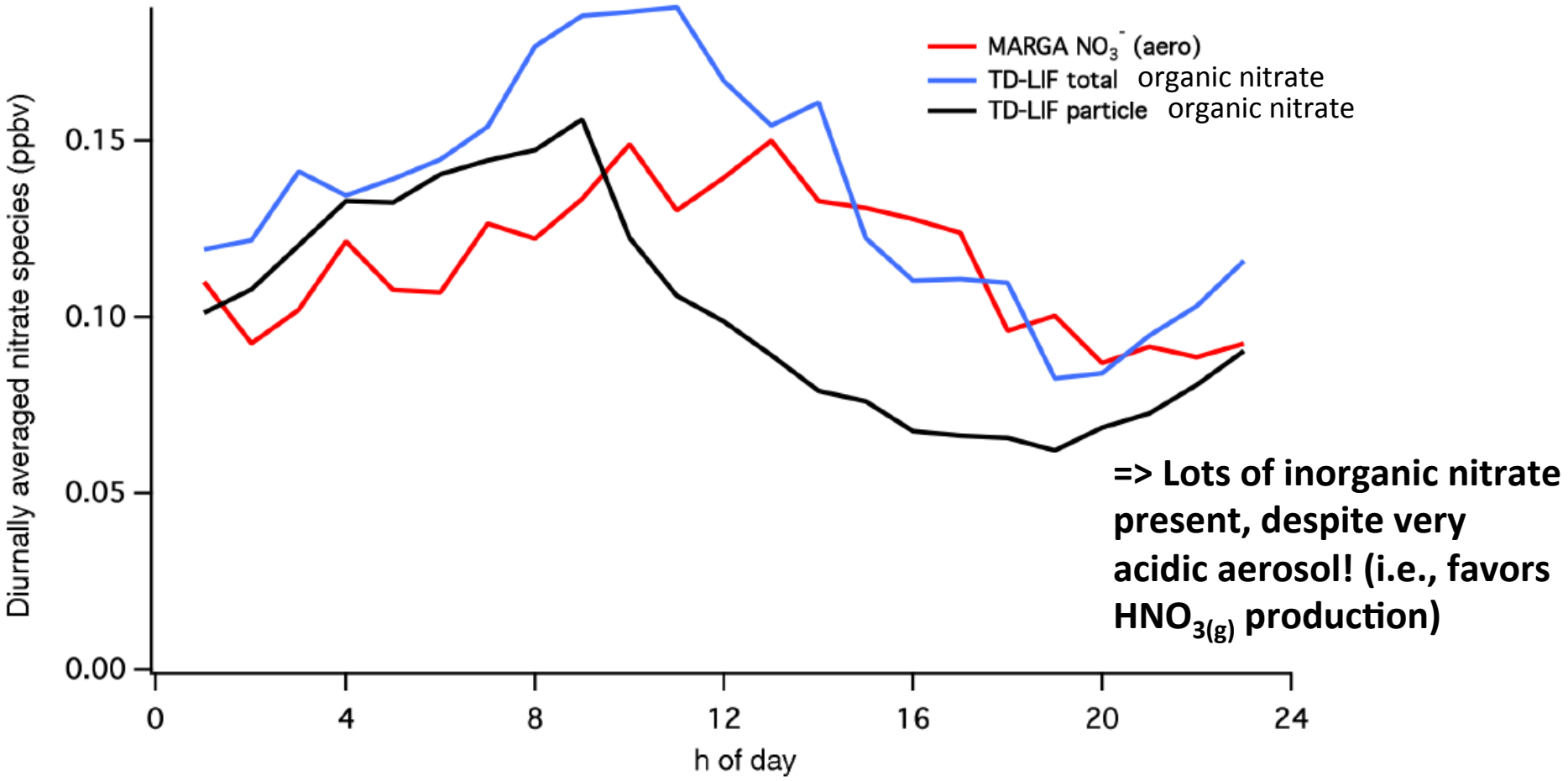
$C_5H_9NO_4$



Possibility of hydrolysis reactions: $RONO_2$ => HNO_3

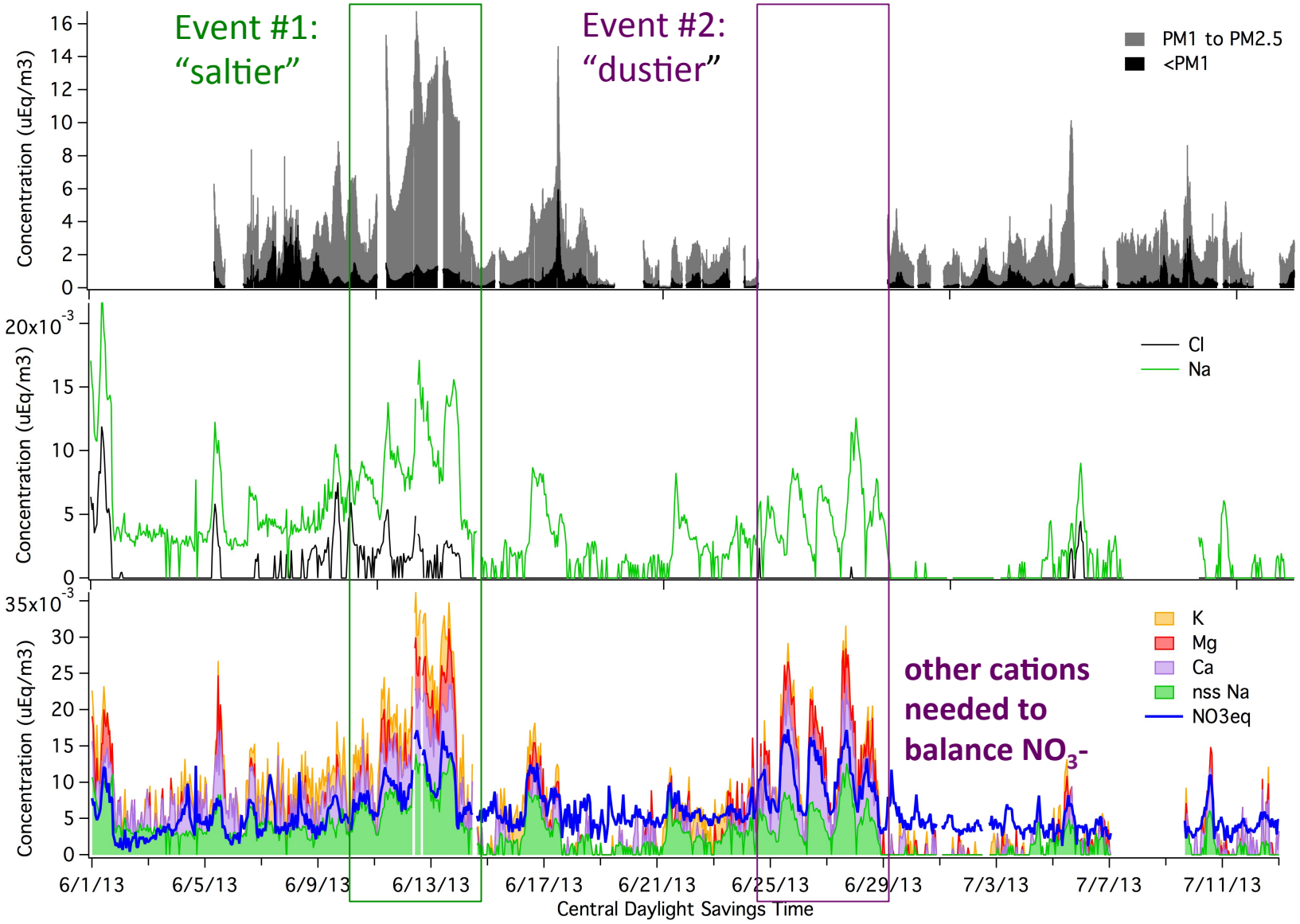
- Remember: hydrolysis is fast for <u>tertiary</u> nitrates but slow for secondary or primary nitrates
  - Supported by chamber expts showing loss of (selected) organonitrates (Liu et al 2012, Boyd et al 2015) and field studies (Day et al 2010; Browne et al 2013) showing high $HNO_3/RONO_2$ ratio
- This is a mechanism by which particle-phase nitrate could be re-released to gas-phase HNO_3!
- NOTE: Because of radical attack mechanisms, daytime (OH-initiated) nitrates are much more likely to be tertiary than nighttime (NO_3) – NO_3 chemistry makes organonitrates with more staying power!

And there are more possible NOx fates: Similar magnitude inorganic $NO_3^-{}_{(aq)}$ aerosol to organoNO_3!



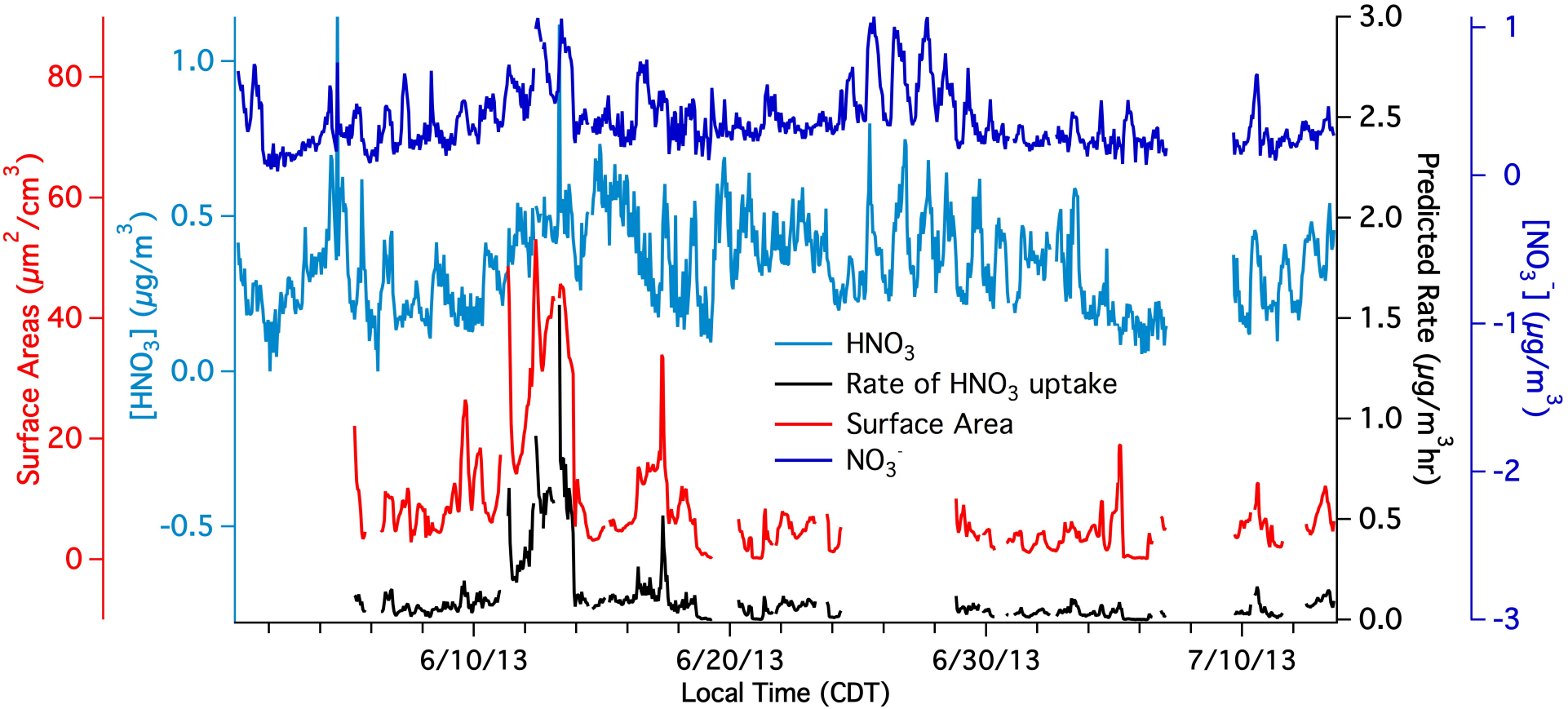
=> Lots of inorganic nitrate present, despite very acidic aerosol! (i.e., favors $HNO_{3(g)}$ production)

Aerosol inorganic composition is more episodic; shows two clear mineral nitrate events: 6/12-6/14 and 6/25-6/28



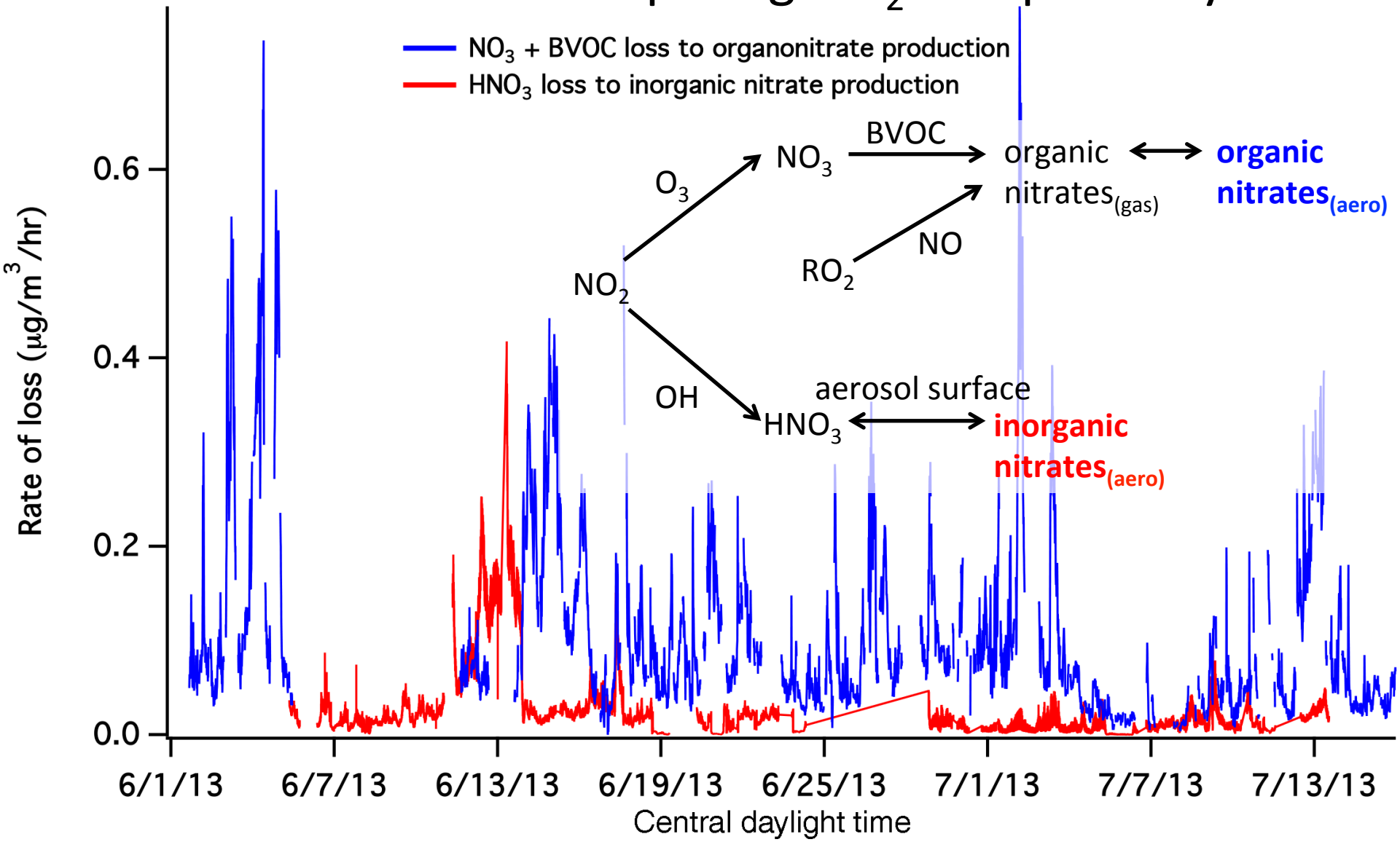
Allen et al., ACP 2015.

Conclusion based on high mineral nitrate concentrations & surface area: Uptake of HNO_3 onto dust produces coarse-mode inorganic nitrate



estimated rate based on γ = 0.1

Relative rates of competing NO_2 loss pathways

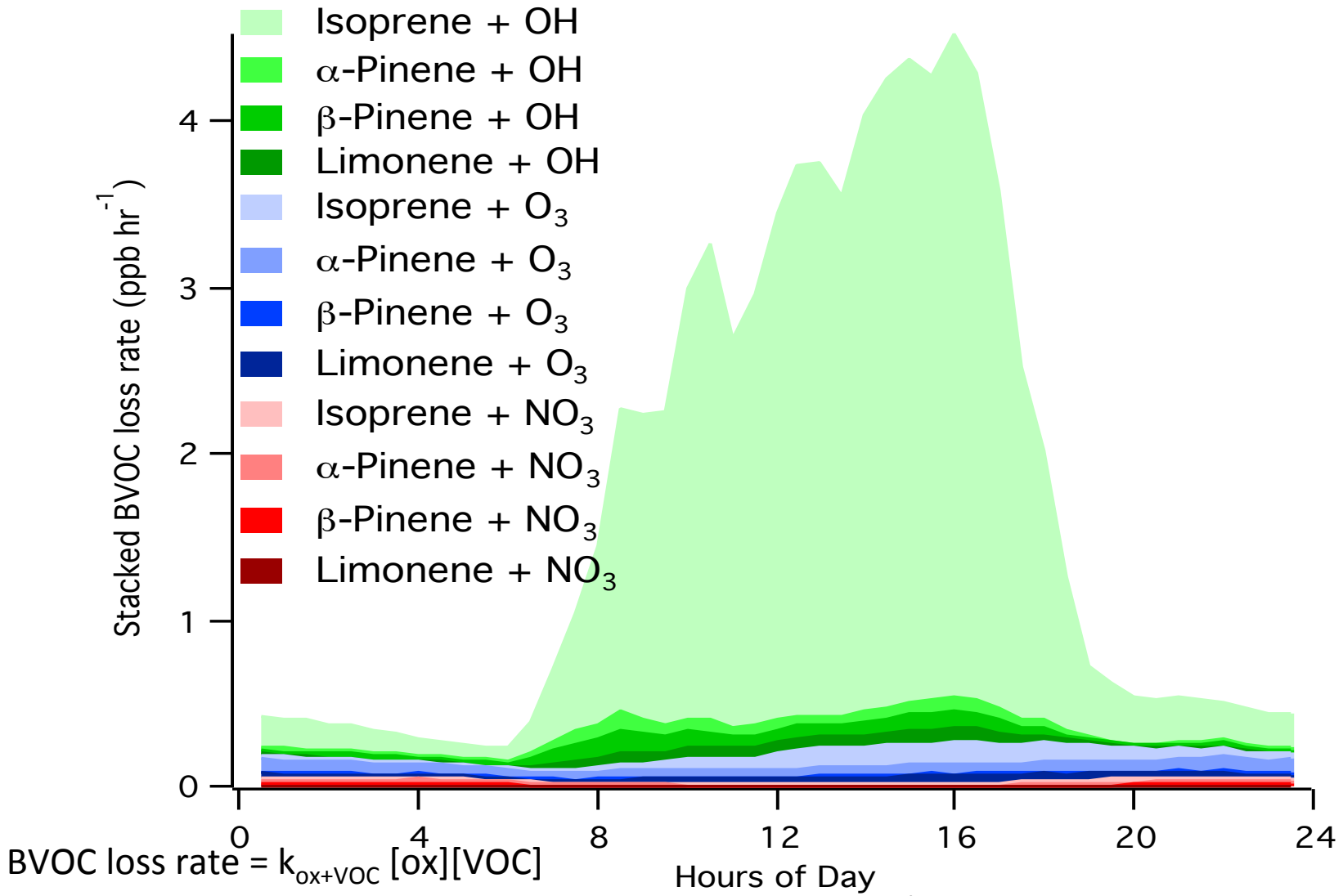


1 ppb NO_3 = 2.5 ug/m^3

SOAS field study reactive N conclusions

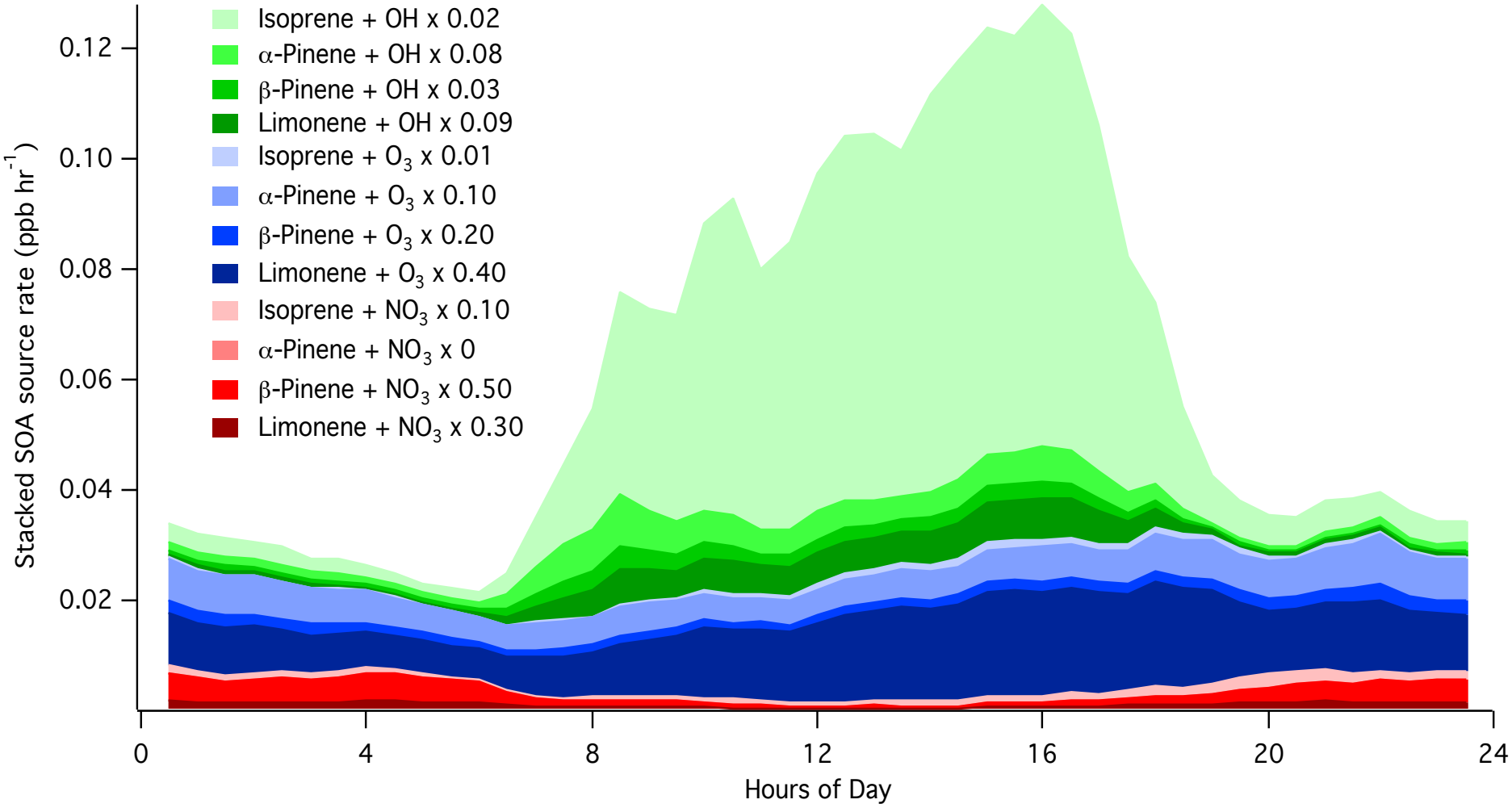
- Nitrate aerosol is an important component of ambient PM, even outside of urban centers; NO_3 initiated chemistry is not only at night
- Surface concentrations of organic/inorganic nitrate aerosol were comparable on average at SOAS (inorganic is mostly >PM_1)
- Campaign avg rate of organonitrate formation: 0.25 ppb hr^{-1}, max 2 ppb hr^{-1} ; mostly NO_3+monoterps
- Campaign avg rate of inorganic nitrate formation: 0.25 ppb hr^{-1}, max 3.8 ppb hr^{-1}; mostly dust events
- Some organic nitrates may convert to HNO_3 via hydrolysis; NO_3-initiated less likely to hydrolyze than OH-initiated products

Future work: Building a SOAS SOA budget: How much of BVOC losses goes to OH, O_3, NO_3



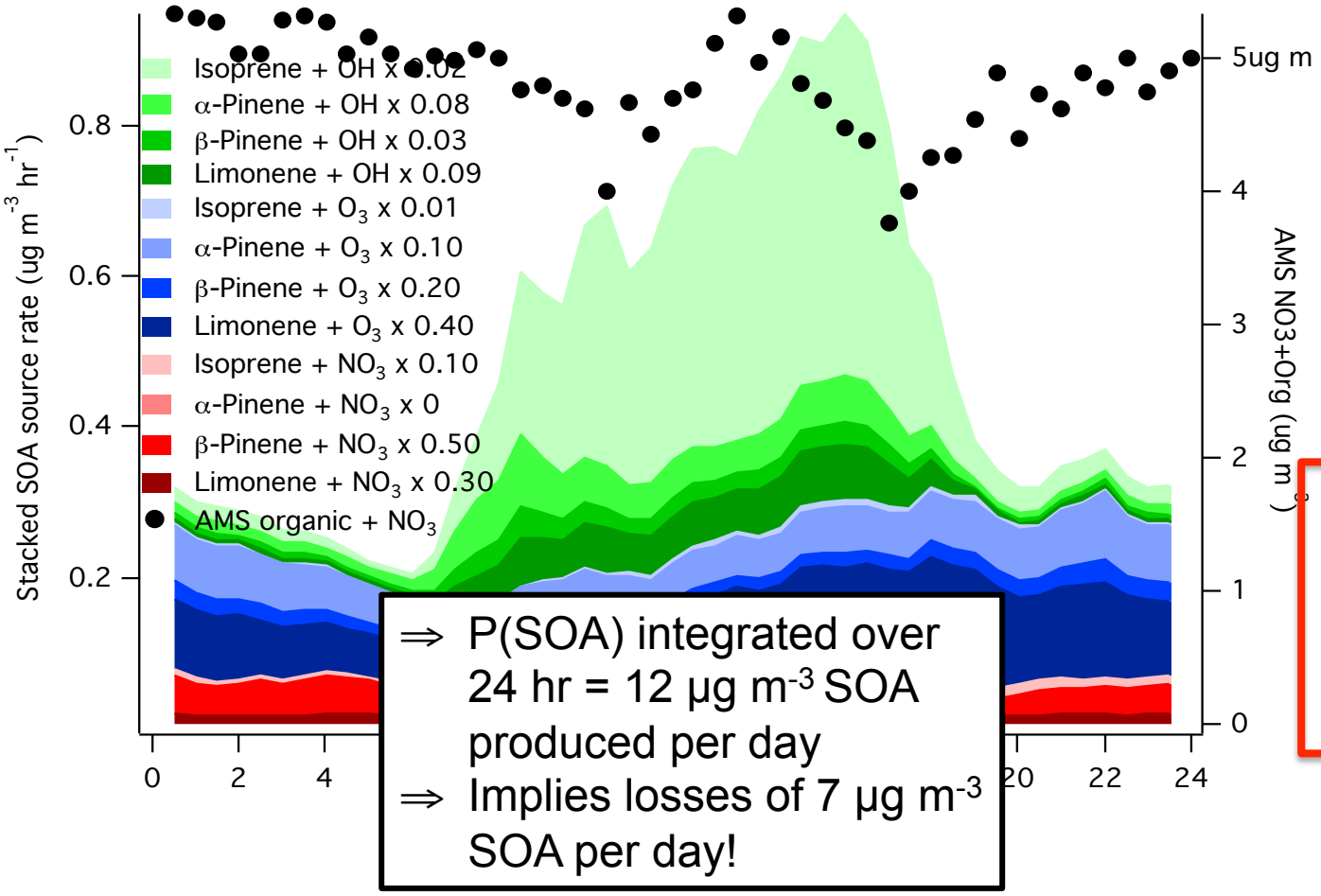
BVOC loss rate = k_{ox+VOC} [ox][VOC]

Future work: Building a SOAS SOA budget: Estimate SOA source from each BVOC rxn with OH, O_3, NO_3



SOA source rate = $Y_{SOA}\ k_{ox+VOC}\ [ox][VOC]$

Future work: Building a SOAS SOA budget: Comparing estimated SOA source with observed loading implies rapid losses



⇒ P(SOA) integrated over 24 hr = 12 μg m^{-3} SOA produced per day

⇒ Implies losses of 7 μg m^{-3} SOA per day!

- Using measured [oxidant]s, [BVOC]s, and literature reaction rates and SOA yields
- Assumes MW = 150 g mol^{-1} for isoprene products, 250 g mol^{-1} for terpene products
- Losses of aerosol-phase organonitrate, entrainment, deposition are not taken into account

Future work: Building a SOAS SOA budget: Use a mixed-layer model to simulate diurnal PBL dynamics

$$\frac{dC_{OA}}{dt} \simeq \overbrace{\frac{w_e \Delta OA_{BG}}{h}}^{OA_{BG}\text{-entrainment}} + \sum_i X_{p,i} \left[\overbrace{\frac{w_e \Delta C_i}{h}}^{C_i\text{-entrainment}} + \overbrace{\sum_j \alpha_i k_j \langle TERP \rangle \langle OX_j \rangle}^{C_i\text{-chemistry}} \right]$$

Future work: Building a SOAS SOA budget: Use a mixed-layer model to simulate diurnal PBL dynamics

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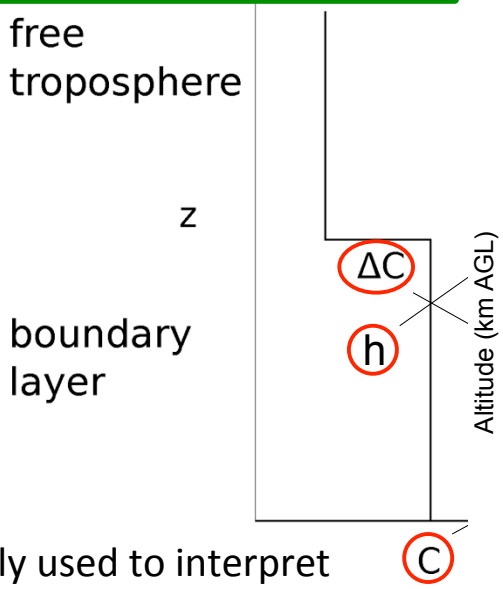
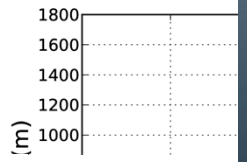
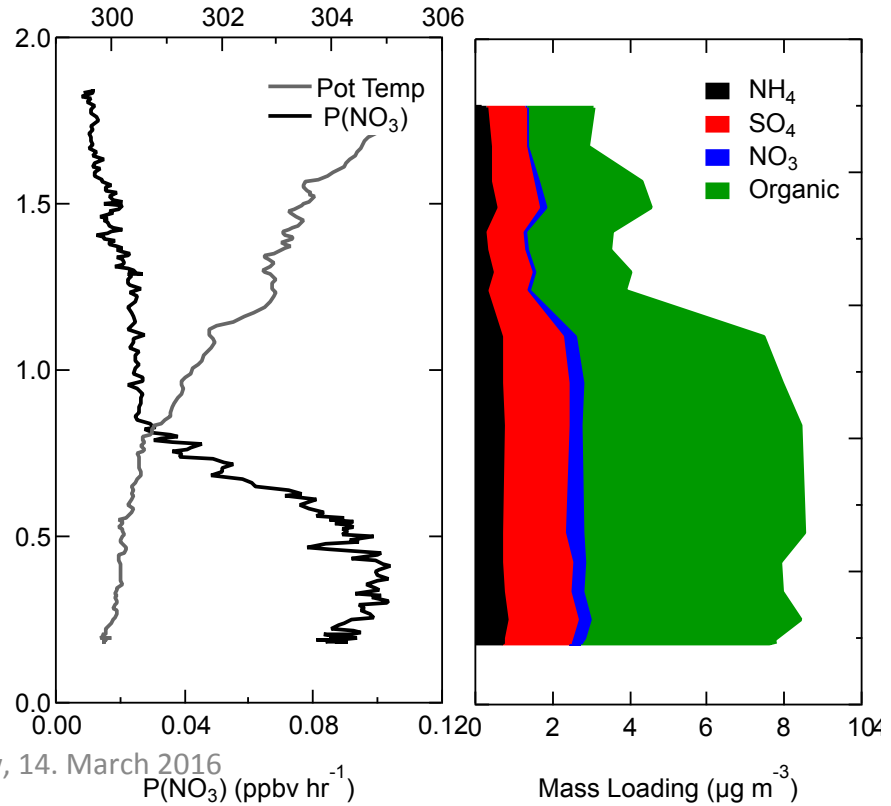


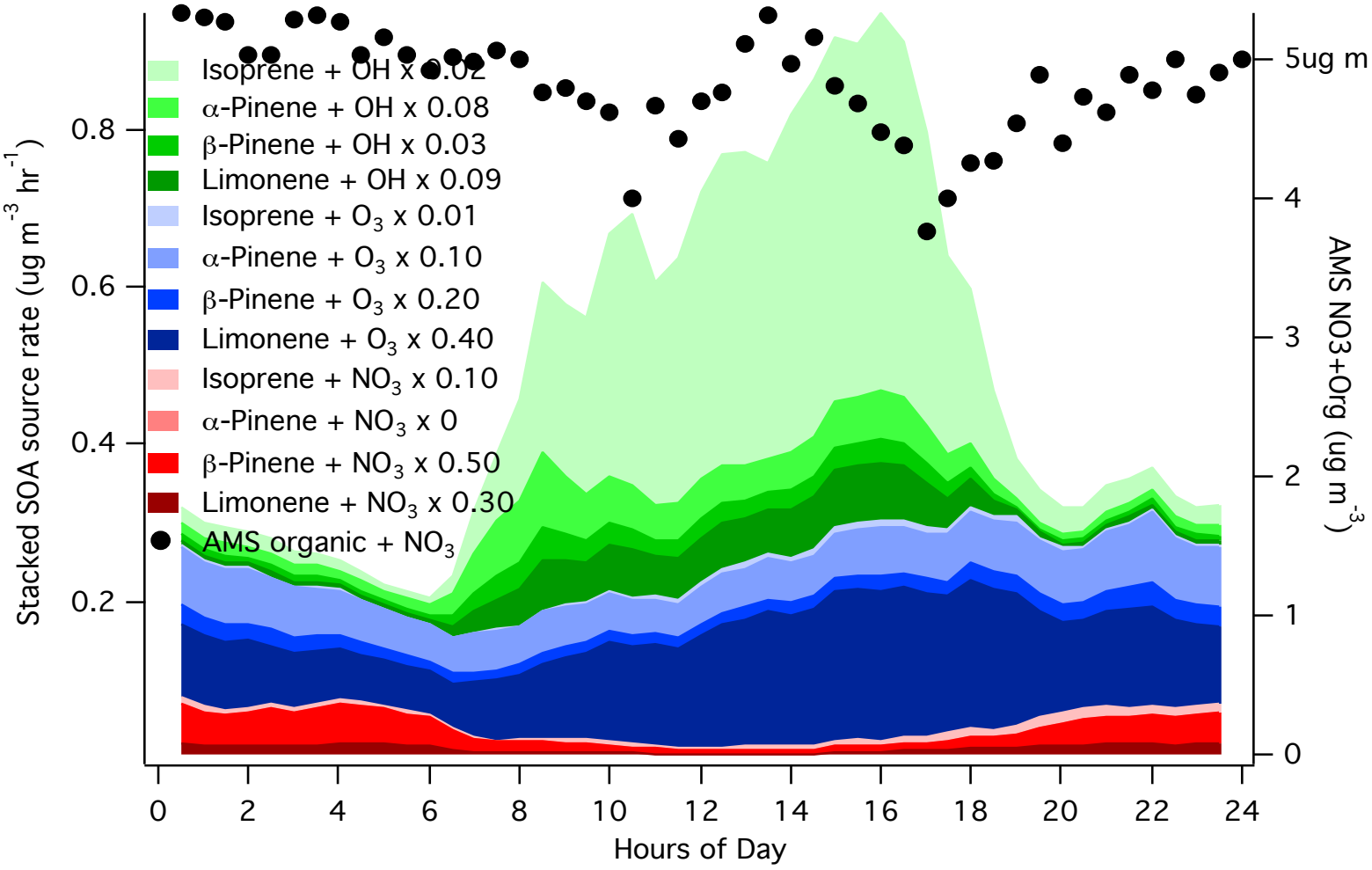


Potential Temperature (K)



Model has been successfully used to interpret other field campaigns, e.g. OP3 (Janssen et al., ACP 2013); Entrainment figure courtesy R. Janssen & J. Vilà, Wageningen Univ.

Future work: Building a SOAS SOA budget **GOAL:** accurately simulate SOA sources and sinks to capture the observed (lack of) diurnal variation in OA



Thanks to:

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- **EPA STAR program** grant #83539901 enabled Team Reed to be at SOAS!

Graduate student at Caltech

Graduate student at UC Irvine

Helping Portland figure out its airborne heavy metal problem