United States Environmental Protection Agency

Using SOAS & related field study data for scientific and regulatory modeling

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Using SOAS & related field study data for scientific and regulatory modeling:

How field and laboratory data has moved us from surrogates to explicit SOA mechanisms

Office of Research and Development
National Exposure Research Laboratory, United States Environmental Protection Agency

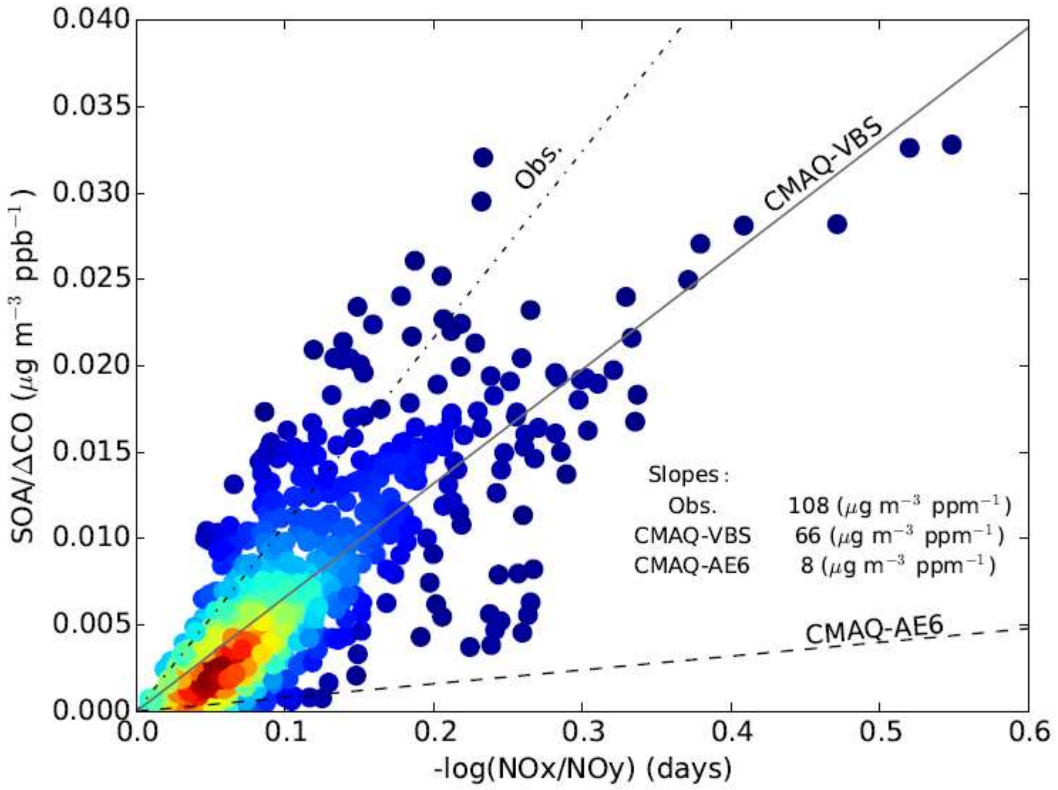
EPA STAR, 15 March 2016

Development of State of the Science SOA Models

- CMAQ model is often used for regulatory decision making in a relative sense (for ozone, SO_2, etc)
- Current regulatory uses do not specifically focus on SOA
  - Large uncertainties in anthropogenically dominated locations
  - More mechanistic information known in BVOC dominated locations (such as the southeast United States)
- Future lower $PM_{2.5}$ NAAQS, component specific $PM_{2.5}$ standards, or climate relevant work could require mechanistic SOA models

SOA Predictions During CalNex 2010

(Woody et al. 2015 ACPD)



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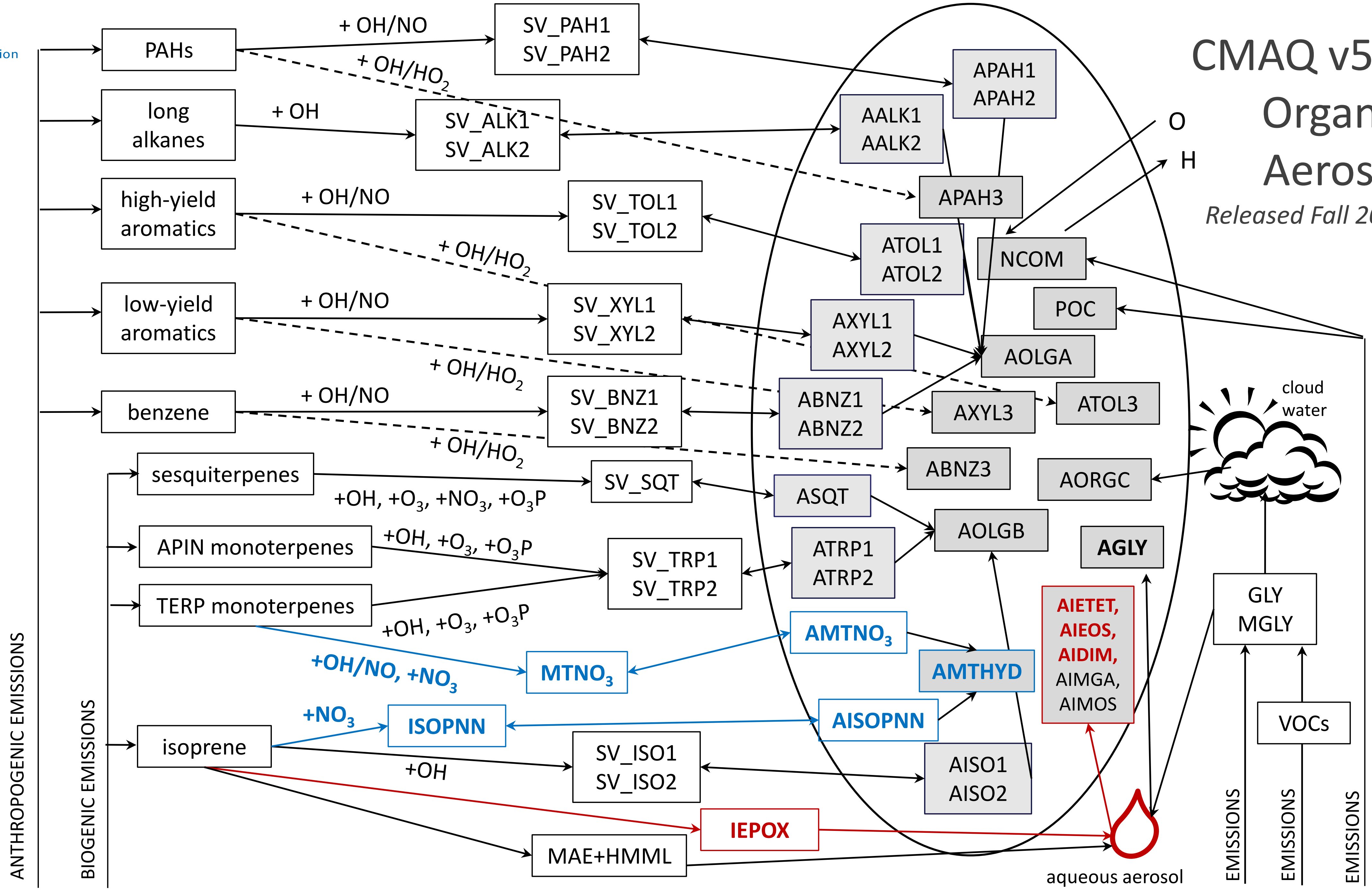
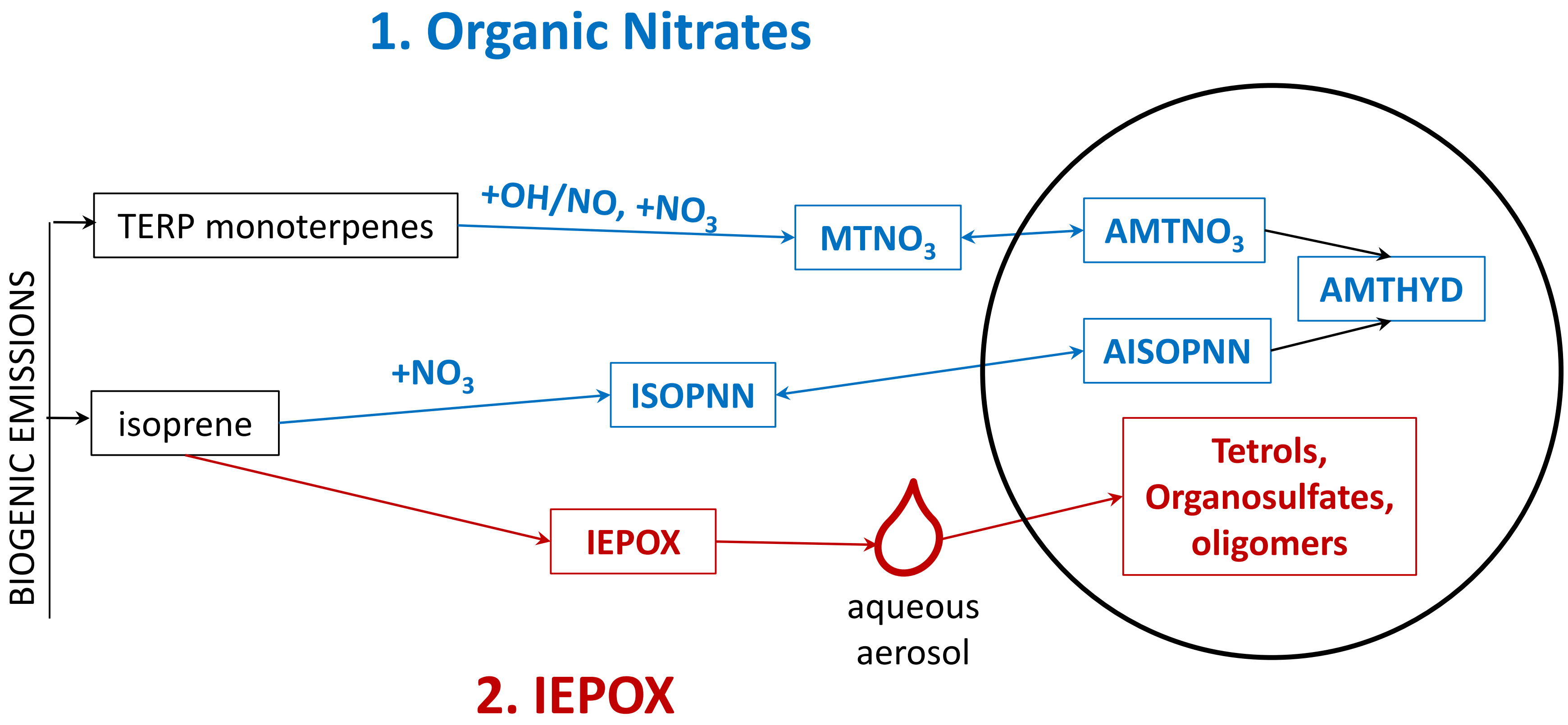
CMAQ v5.1 Organic Aerosol

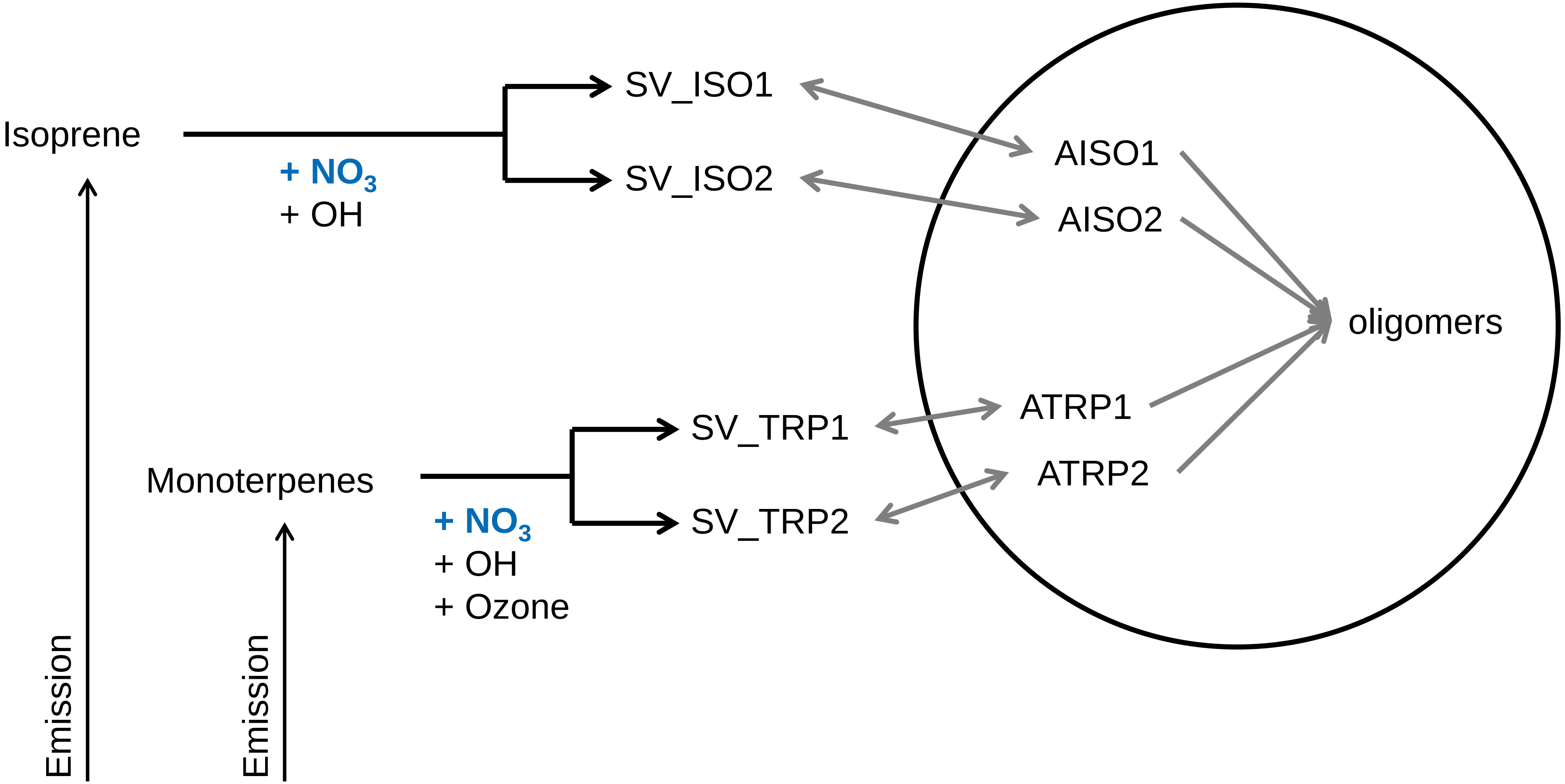
Released Fall 2015



Pathways to SOA in CMAQ informed by SOAS

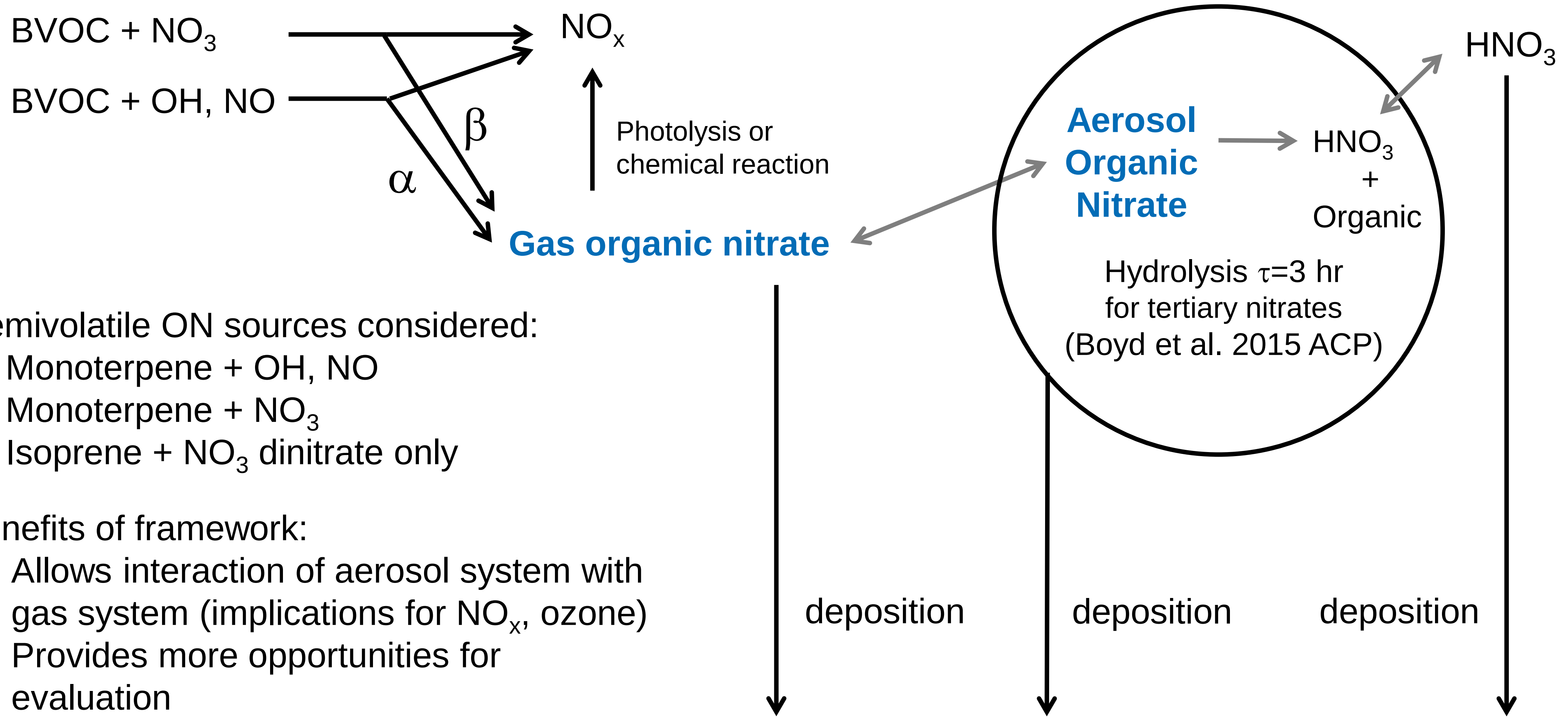


Traditional BVOC+NO_3 OA model



Monoterpenes: Carlton et al. 2010 ES&T
Isoprene: v5.1 unpublished

Revised organic nitrogen SOA model



Semivolatile ON sources considered:

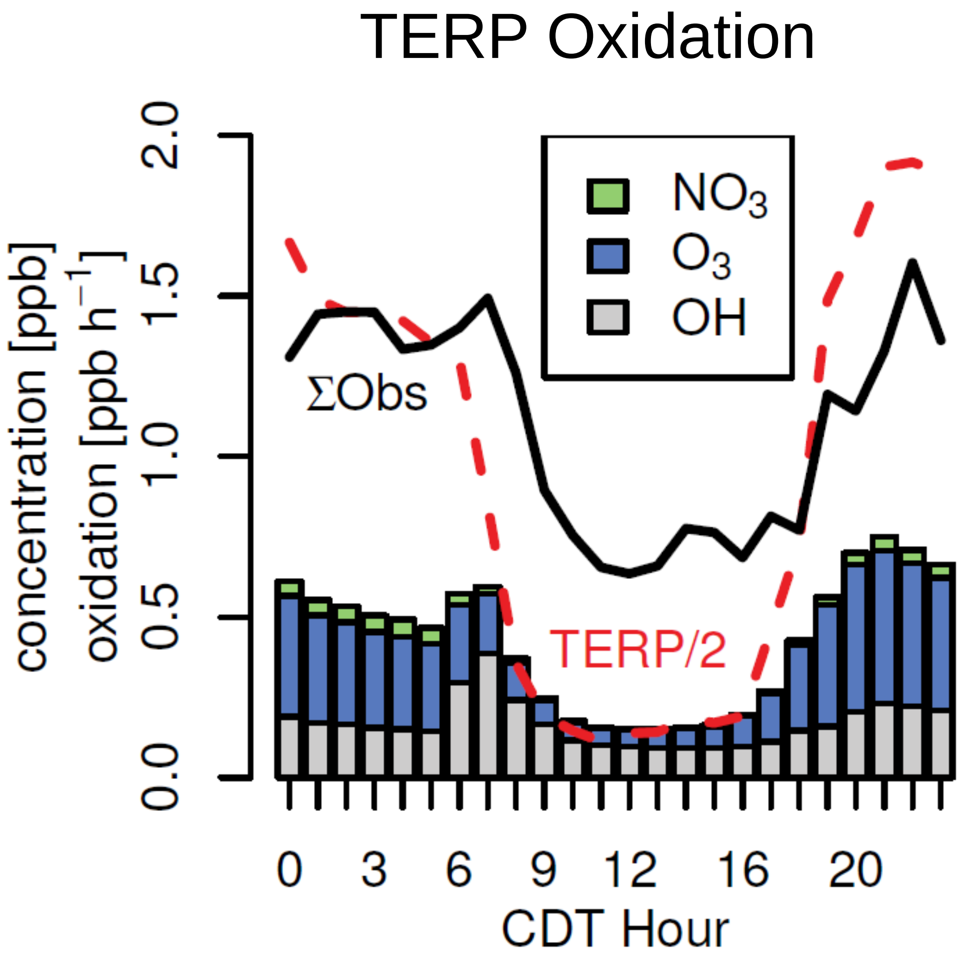
- Monoterpene + OH, NO
- Monoterpene + NO_3
- Isoprene + NO_3 dinitrate only

Benefits of framework:

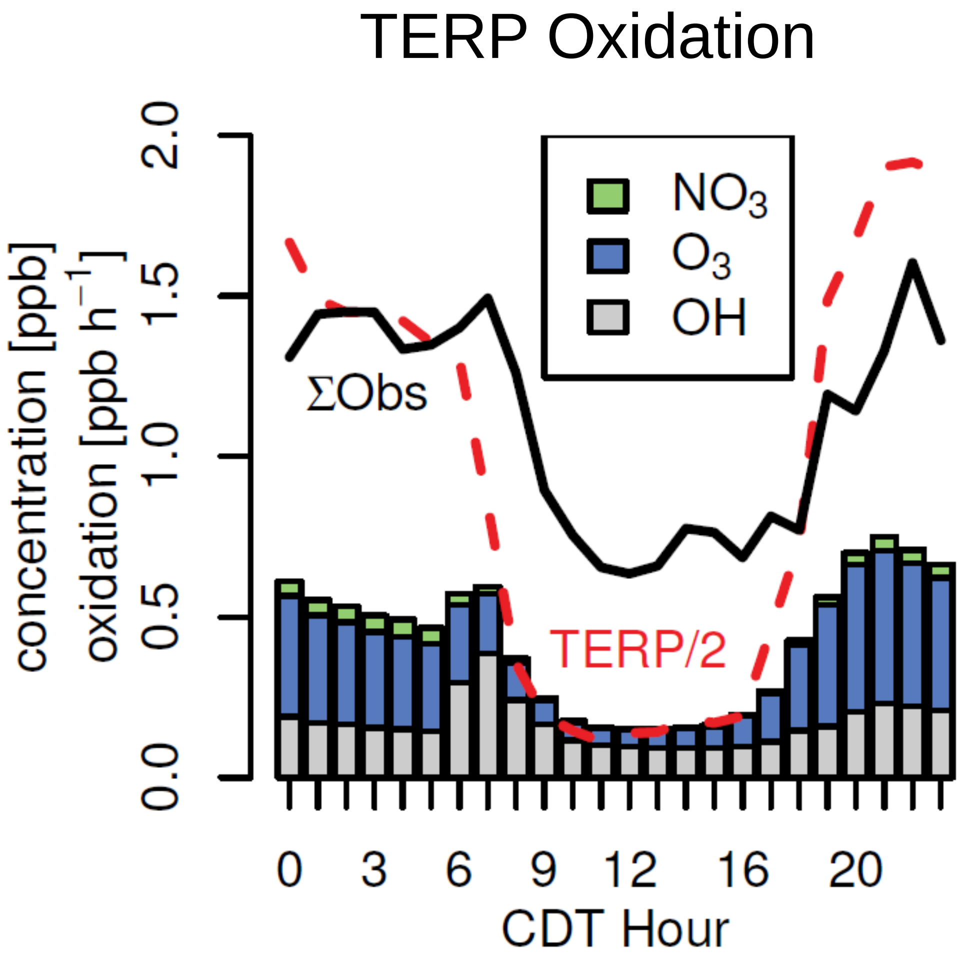
- Allows interaction of aerosol system with gas system (implications for NO_x, ozone)
- Provides more opportunities for evaluation

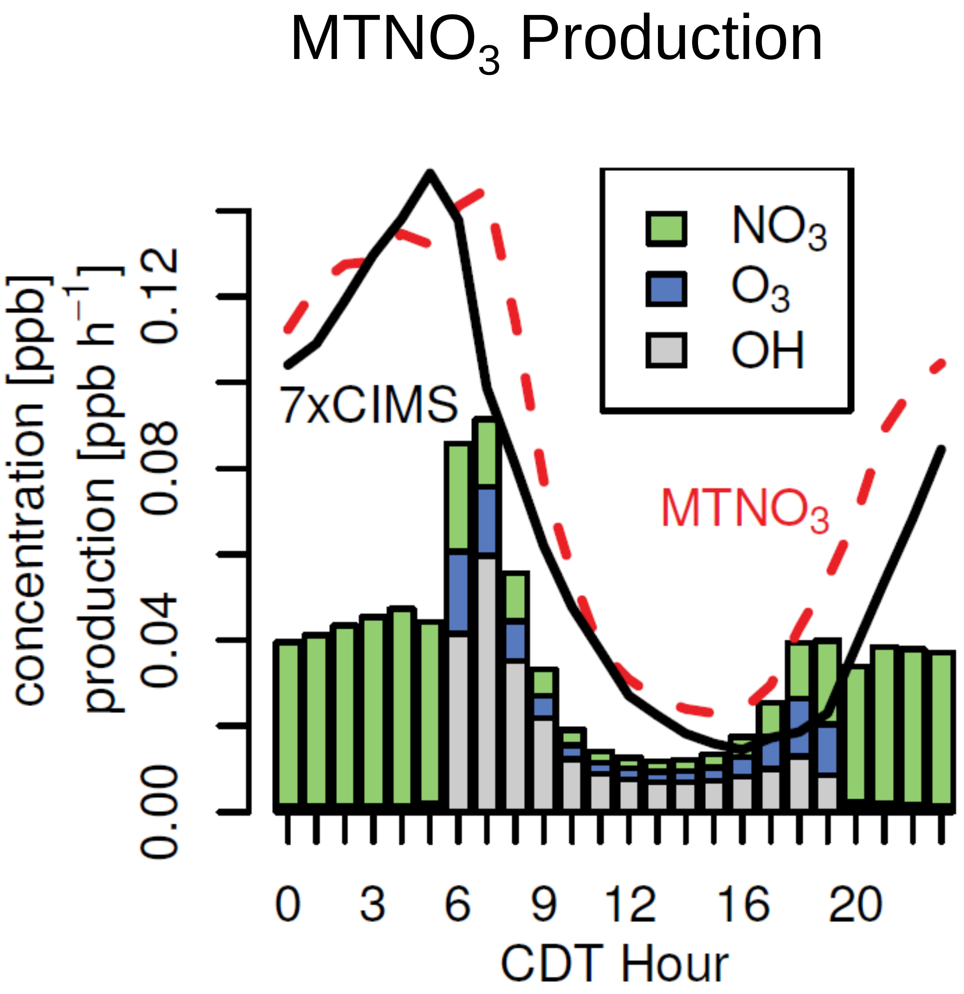
Pye et al. 2015 ES&T

O_3 is the dominant nocturnal oxidant



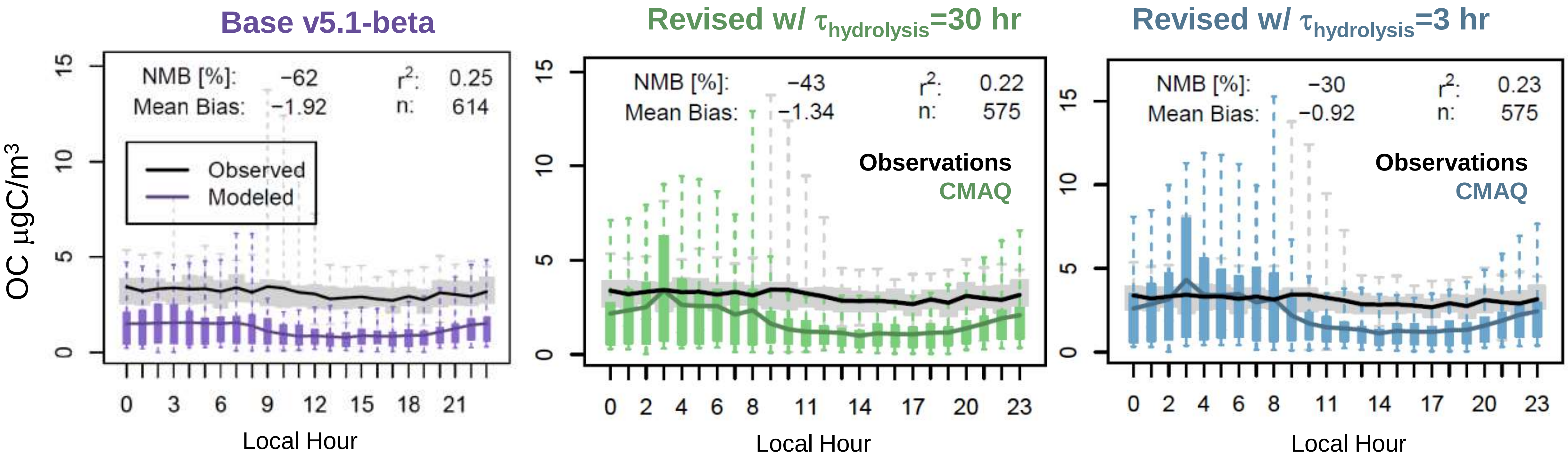
NO_3 is the dominant ON source





* CIMS signal is one subset of $MTNO_3$

OC predicted at CTR June 2013



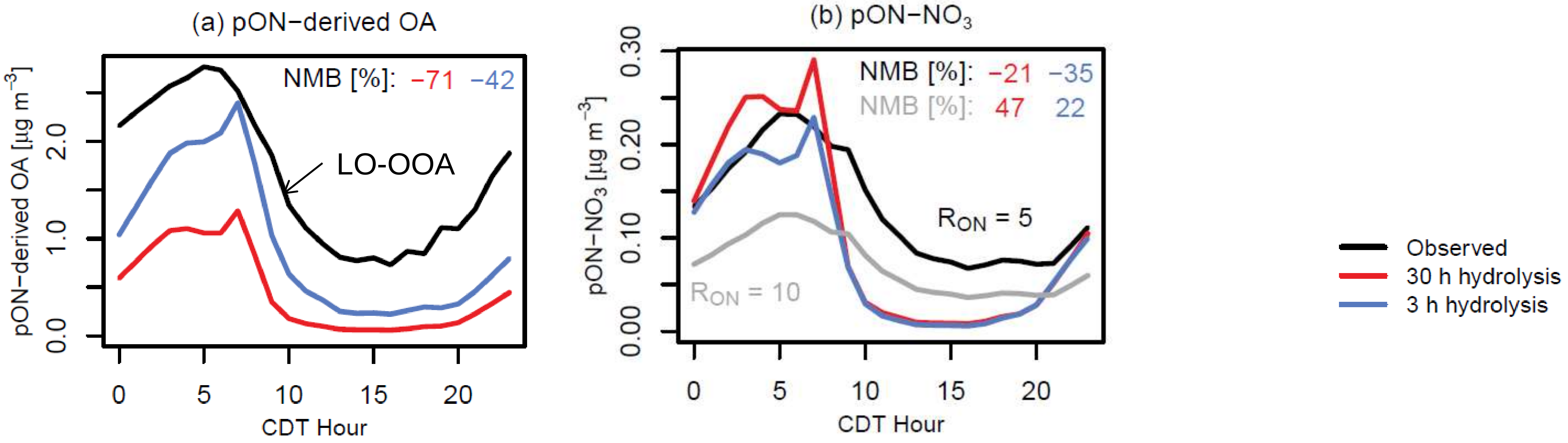
Bias in OA vs AMS: -35% (-1.93 μg/m³)

Bias in OA vs AMS: -23% (-1.26 μg/m³)

Faster hydrolysis consistent with observations

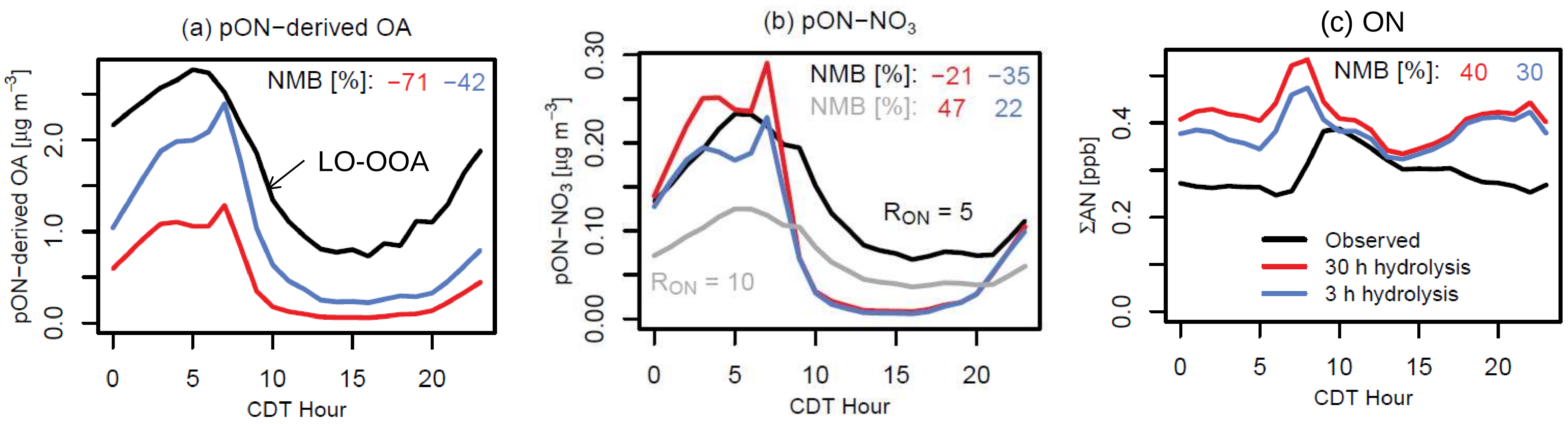
- Increasing the hydrolysis rate increases the magnitude of modeled LO-OOA

Faster hydrolysis consistent with observations



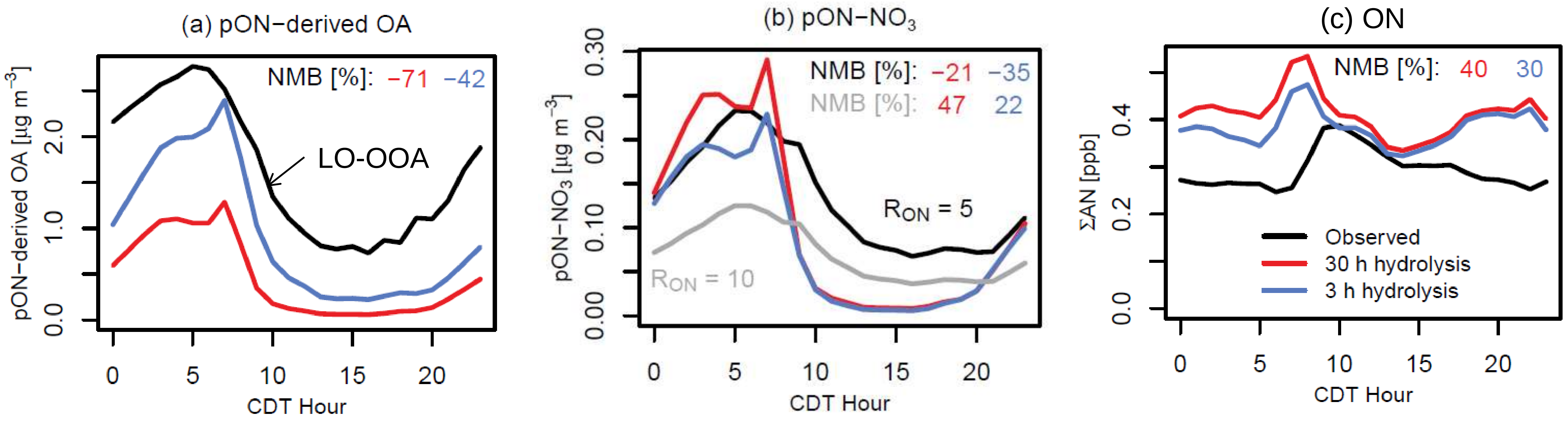
- Increasing the hydrolysis rate increases the magnitude of modeled LO-OOA
- Faster hydrolysis improves the speciation of LO-OOA

Faster hydrolysis consistent with observations



- Increasing the hydrolysis rate increases the magnitude of modeled LO-OOA
- Faster hydrolysis improves the speciation of LO-OOA
- Faster hydrolysis improves the magnitude of gas-phase organic nitrates

Faster hydrolysis consistent with observations



- Increasing the hydrolysis rate increases the magnitude of modeled LO-OOA
- Faster hydrolysis improves the speciation of LO-OOA
- Faster hydrolysis improves the magnitude of gas-phase organic nitrates

40% of LO-OOA not accounted for

IEPOX SOA

- Included in all research and regulatory mechanisms of CMAQ as of v5.1
- Modeled as reactive uptake (Pye et al. 2013 ES&T)

$$\text{epoxide(g)} \xrightarrow{k_{het}} \text{aerosol}$$

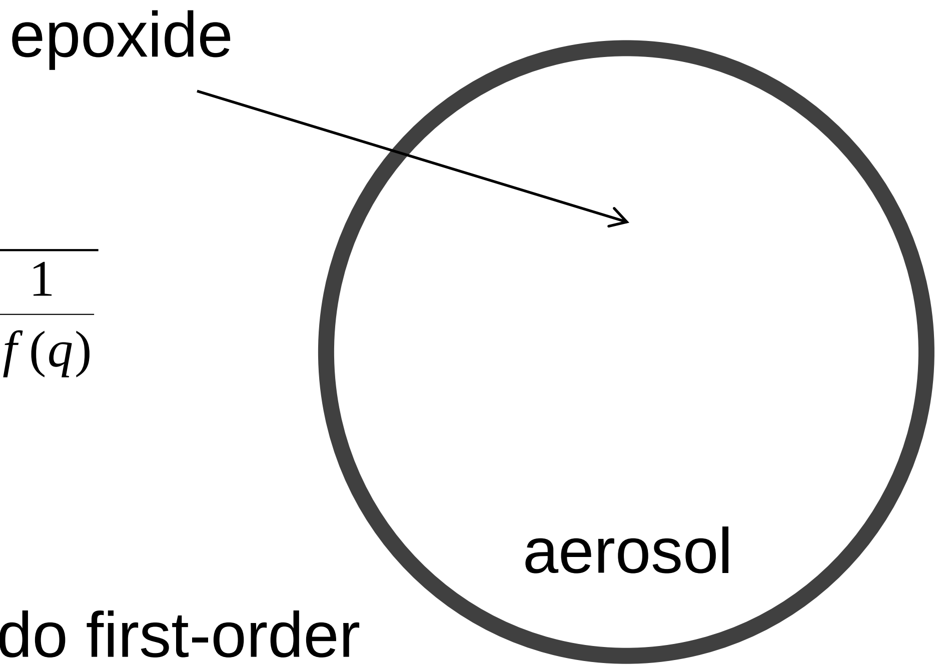
$$k_{het} = \frac{A}{\frac{r_p}{D_g} + \frac{4}{\nu \gamma_{epoxide}}}$$

$$\gamma = \frac{1}{\frac{1}{\alpha} + \frac{\nu}{4H^*_{eff} RT \sqrt{D_a k_{particle}}} \cdot \frac{1}{f(q)}}$$

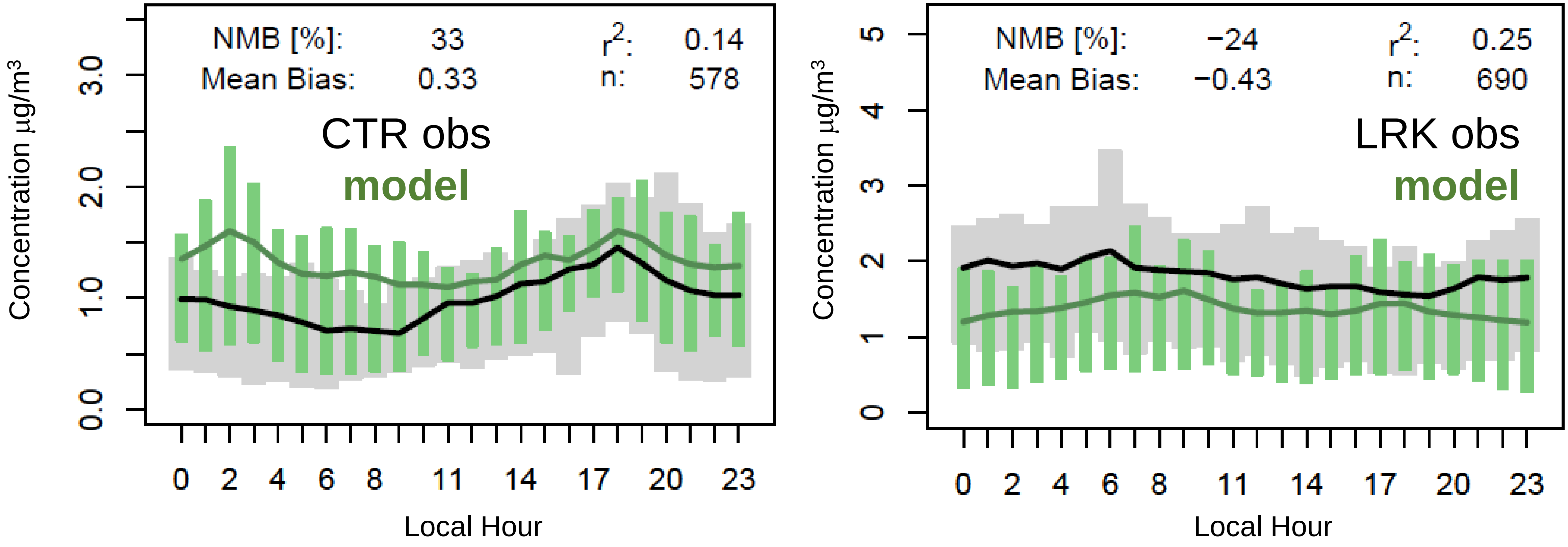
$$f(q) = \coth(q) - \frac{1}{q}$$

$$q = r_p \sqrt{k_{particle} / D_a}$$

Pseudo first-order particle-phase reaction rate constant



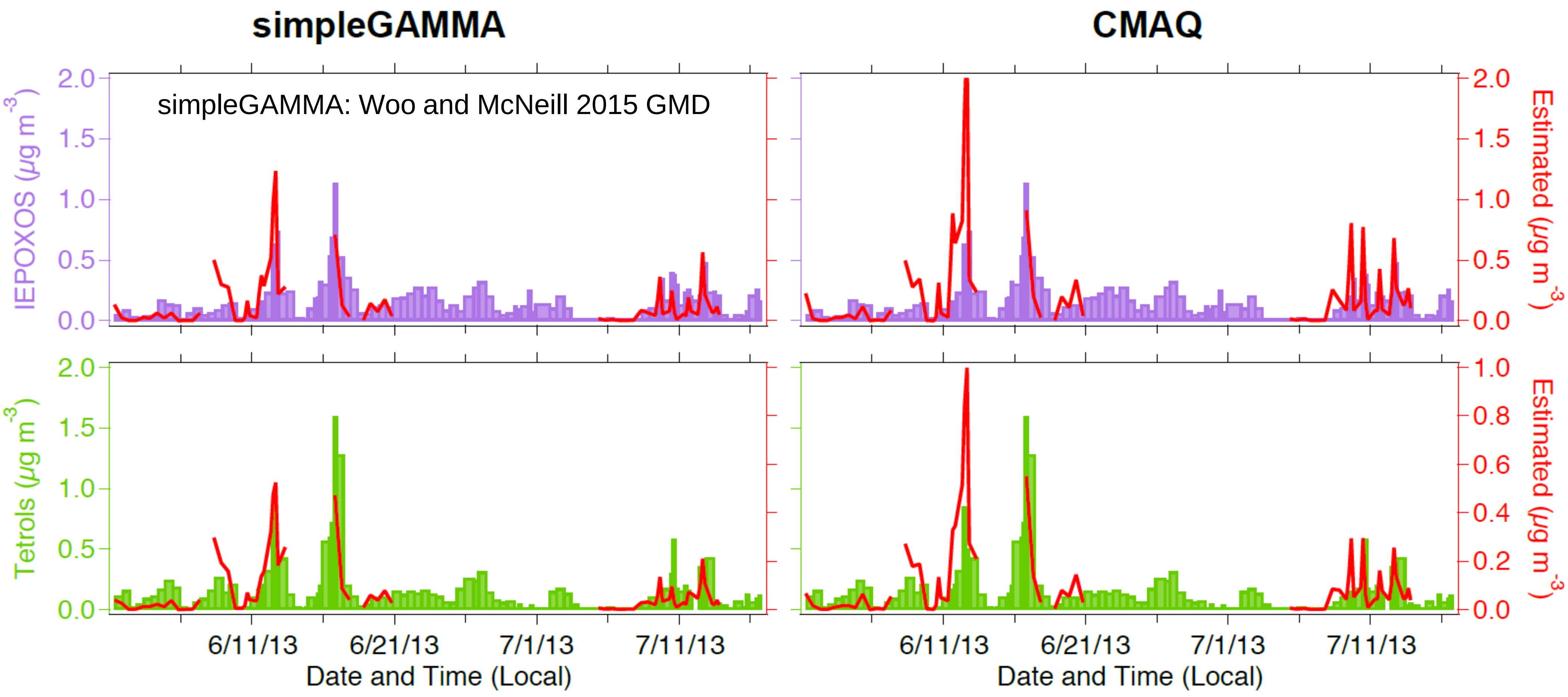
CMAQ Predictions of IEPOX-OA



- CMAQ predictions reproduce the observed correlation with sulfate

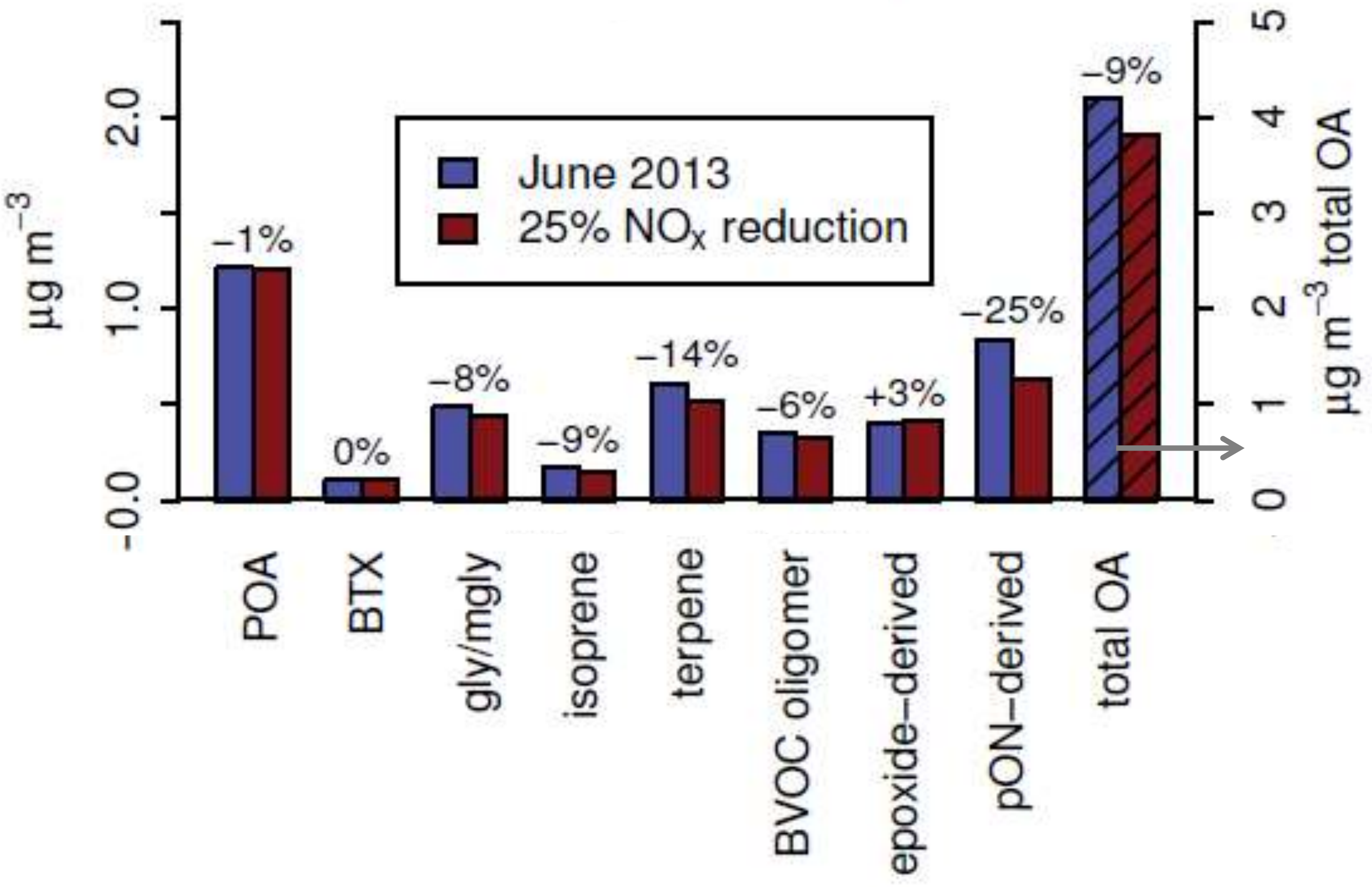
Modeling of the SOAS-LRK Site

Budisulistiorini et al. in prep



- Models reproduce observed correlation of IEPOX-derived species (tetrols+organosulfates) with aerosol volume and surface area and lack of correlation $k_{particle}$

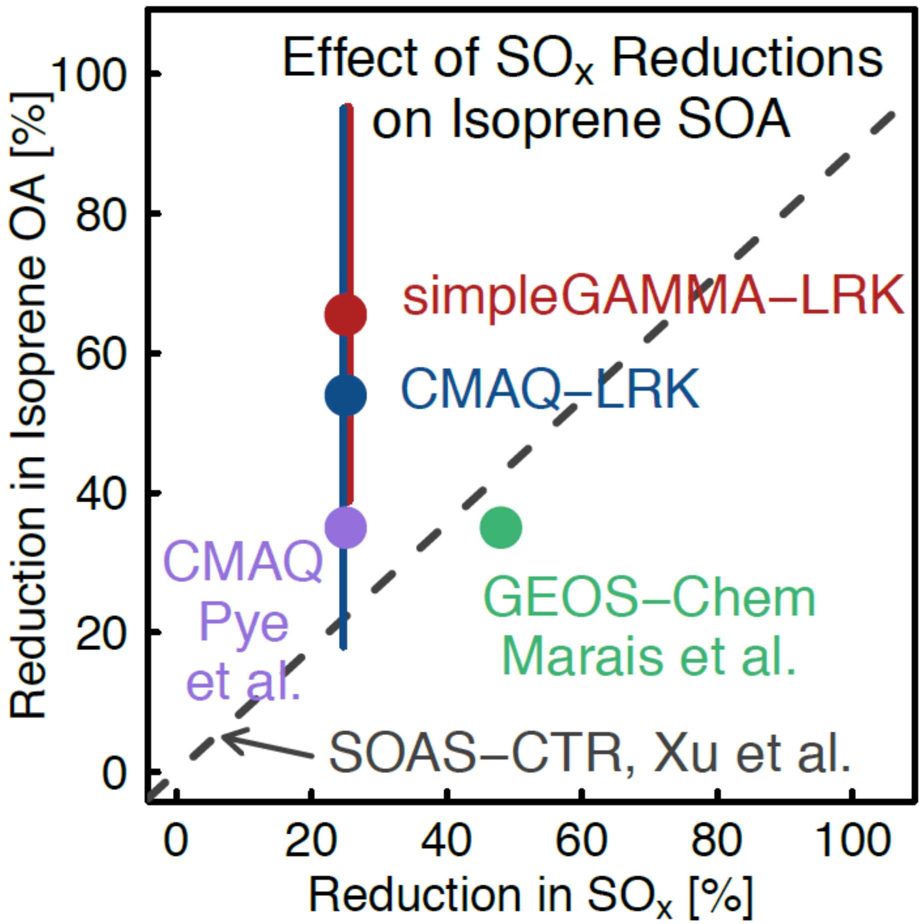
NO_x emission reduction leads to OA reduction



Pye et al. 2015 ES&T

SO_x Emission Reduction Leads to Isoprene SOA Reduction

Budisulistiorini et al. *in prep.*



Pye et al. 2013 isoprene-OA includes semivolatile and aqueous IEPOX SOA

Marais et al. 2015 isoprene-OA
58% from IEPOX
28% from glyoxal

Conclusions

- Mechanistic SOA parametrizations give us confidence in the predictive capability of models
- For organic nitrate-derived SOA, gas-phase mechanisms should couple with aerosol-phase mechanisms
- CMAQ model predictions are consistent with SOAS observations of NO_y components when particle phase organic nitrates undergo fast reaction (3 h)
- Significant progress has been made in modeling isoprene-OA, but uncertainties exist (e.g. the composition of the isoprene-OA factor)
- NO_x and SO_x emission reductions in the Southeast are expected to reduce SOA

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