Using explicit mechanisms of Secondary Organic Aerosol (SOA) formation and evolution to extrapolate chamber studies to the atmosphere

JOEL THORNTON JOELT@UW.EDU

DEPARTMENT OF ATMOSPHERIC SCIENCES, UNIVERSITY OF WASHINGTON

Guiding Questions

- How do we translate chamber measurements of SOA formation to atmospheric predictions?

- Are current mechanisms of isoprene oxidation capable of explaining volatility-driven (non-aqueous) SOA formation observed in chambers?

- What are the implications of such chemistry for the importance of volatility-driven SOA formation by isoprene?

Chamber studies produce large but variable and dynamic ipSOA yields

Kroll et al 2006
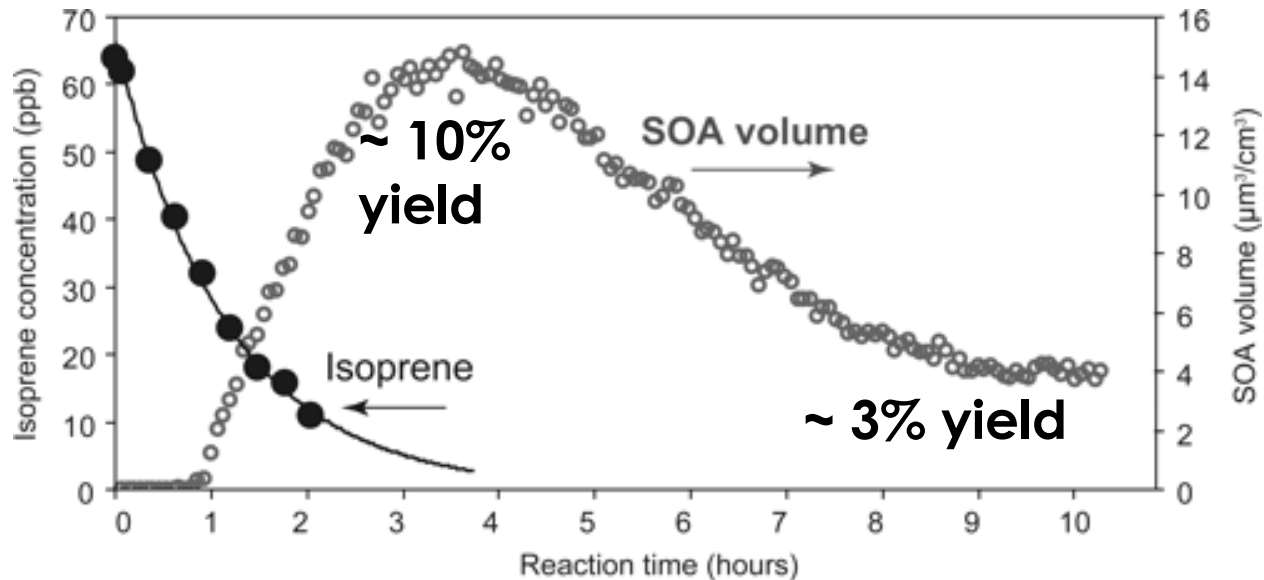
Liu et al 2017 (PNNL-2014)

~ 10% yield

~ 3% yield
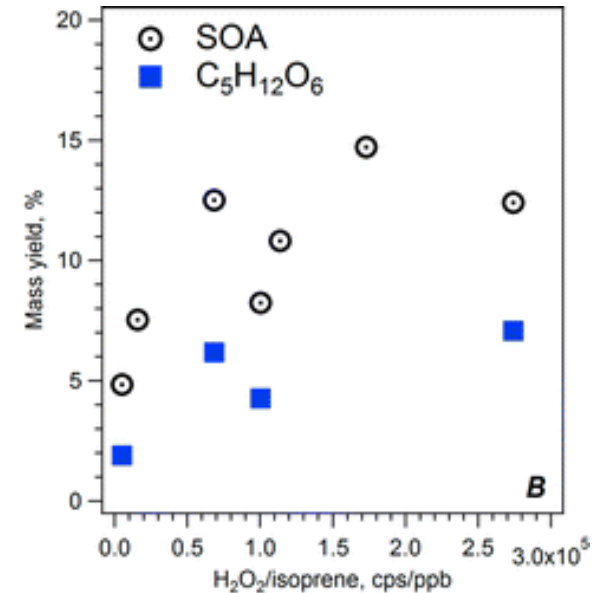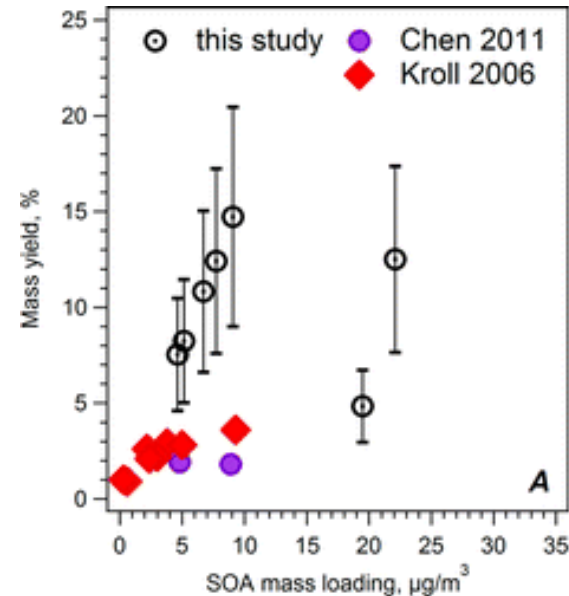
Are these experiments consistent with each other? Chamber radical concentrations? SOA Photolysis? SOA Volatility? Vapor Wall Loss?
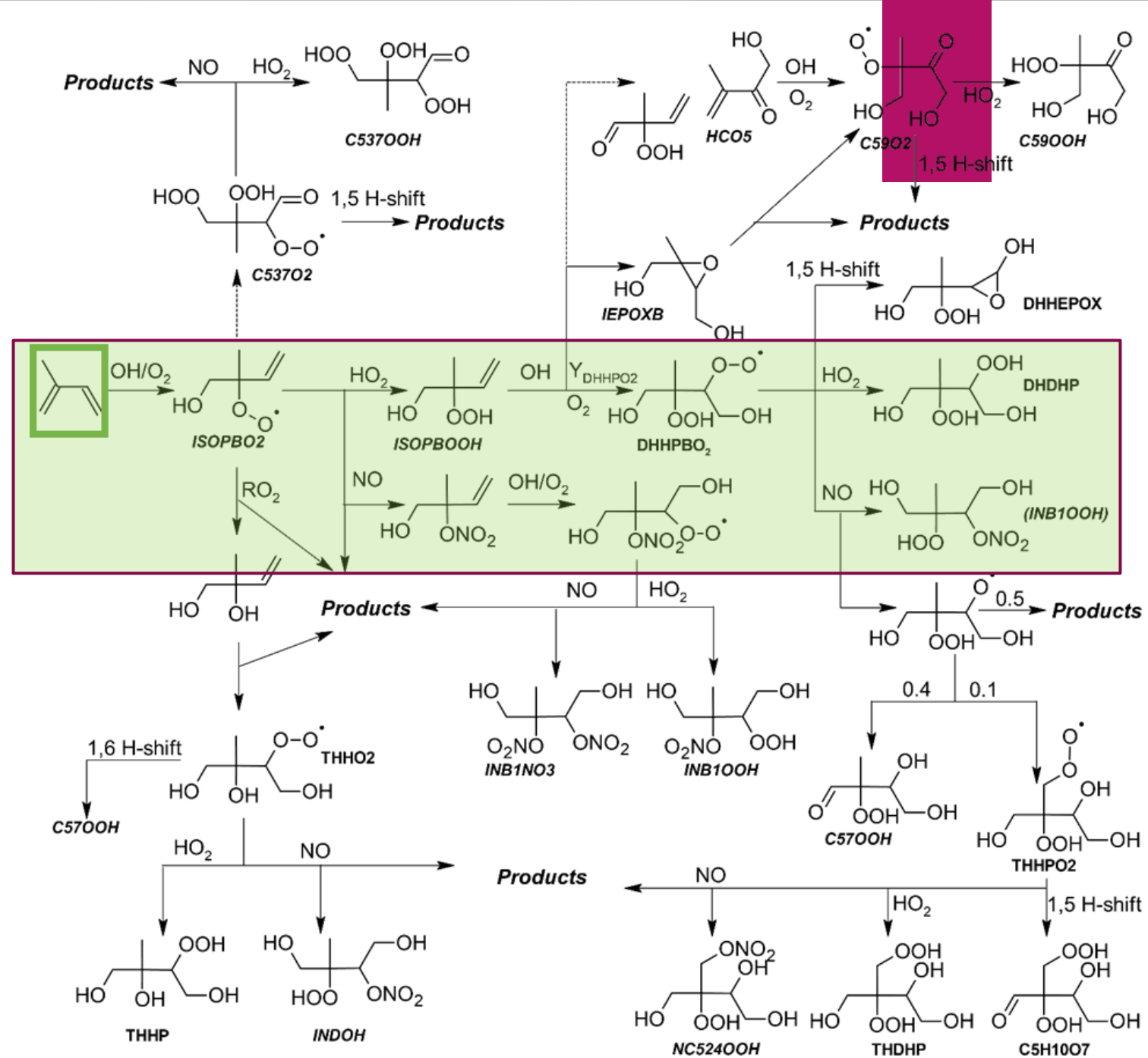
F0AM-WAM Model

Hybrid Master Chemical Mechanism (MCM) with custom additions

Dynamic gas-particle and gas-wall partitioning with structure-based saturation vapor concentrations (c*)

Explicit particle-phase photolysis and accretion chemistry

D'Ambro et al. ES&T 2017
Wolfe et al. GMD 2016

# Chamber experiments (33 total)

**Time-dependent closed system ("Batch")**

Continuous-flow steady-state (CFSS) open system

Caltech (Kroll–2006) and Pacific Northwest National Laboratory (PNNL) ~ 10 m³ Teflon chambers

**All use H_2O_2 as OH source and with and without added NO_x**

Chamber	Type	Run	Isoprene (ppbv)	H_2O_2 (ppmv)	NO (ppbv)	Seed (um³ cm⁻³)	Temperature (°C)
Kroll-2006	Batch*	1	90	3.5	0	N/A	25.4
Kroll-2006	Batch	2	46.1	3.5	0	N/A	25.6
Kroll-2006	Batch	3	23	3.5	0	N/A	26
Kroll-2006	Batch	4	12.2	3.5	0	N/A	25.7
Kroll-2006	Batch	5	63.6	3.5	0	N/A	26.7
Kroll-2006	Batch	6	29.4	3.5	0	N/A	28.7
Kroll-2006	Batch	7	47.8	3.5	0	N/A	26.6
Kroll-2006	Batch	8	41.6	3.5	0	N/A	26.4
Kroll-2006	Batch	9	46.7	3.5	242	4.6	28.3
Kroll-2006	Batch	10	43.5	3.5	496	7.1	28.3
Kroll-2006	Batch	11	42.7	3.5	98	6.4	28.1
Kroll-2006	Batch	12	49.1	3.5	51	6.5	28.2
Kroll-2006	Batch	13	42.7	3.5	337	4.8	28.3
Kroll-2006	Batch	14	42	3.5	708	4.7	27.5
PNNL-2014	CFSS**	1	26	15	0	0.3	25.4
PNNL-2014	CFSS	2	26	10	0	0.3	25.4
PNNL-2014	CFSS	3	26	10	2	0.3	25.4
PNNL-2014	CFSS	4	26	10	5	0.3	25.4
PNNL-2014	CFSS	5	26	10	10	0.3	25.4
PNNL-2014	CFSS	6	26	10	20	0.3	25.4
PNNL-2014	CFSS	7	26	10	50	0.3	25.4
N/A	CFSS	8	26	10	100	0.3	25.4
PNNL-2015	CFSS	9	20	10	0	0.3	25.4
PNNL-2015	CFSS	10	20	2	0	0.3	25.4
PNNL-2015	CFSS	11	20	5	0	0.3	25.4
PNNL-2015	CFSS	12	20	0.5	0	0.3	25.4
PNNL-2018	Batch	1	43.5	7.5	0	0.3	24.0
PNNL-2018	Batch	2	65	7.5	0	0.3	24.0
PNNL-2018	Batch	3	69	7.5	0	0.3	24.0
PNNL-2018	Batch	4	56.5	7.5	0	0.3	24.0
PNNL-2018	Batch	5	51	7.5	0	0.3	24.0
PNNL-2018	Batch	6	57	7.5	0	0.3	24.0
PNNL-2018	Batch	7	48	7.5	0	0.3	24.0

**Comparison to Kroll-2006 without-NO$_x$ Experiments**
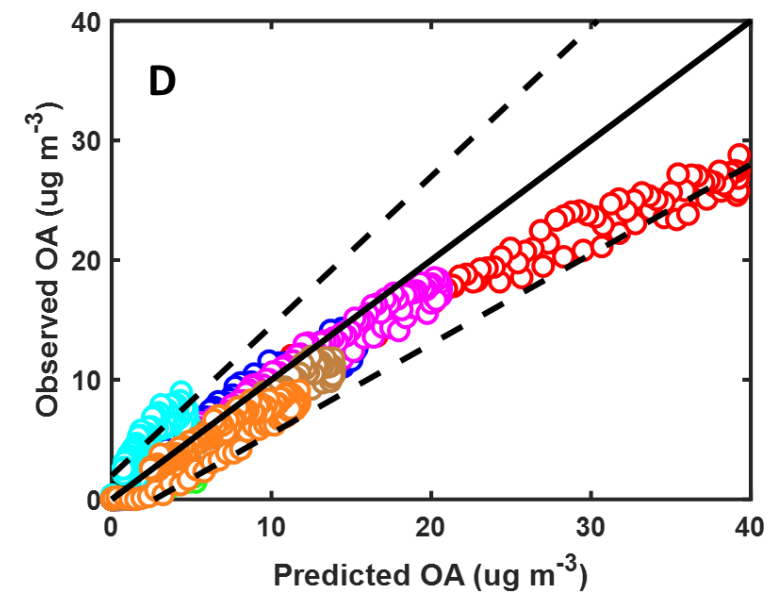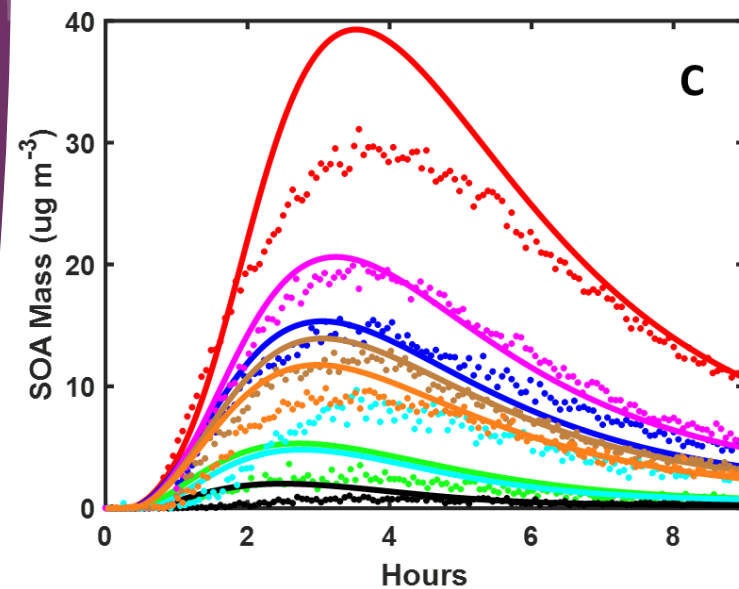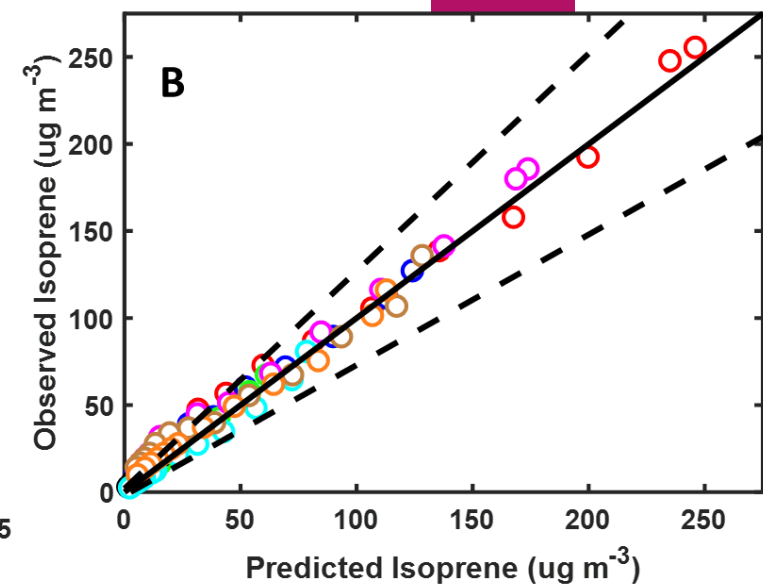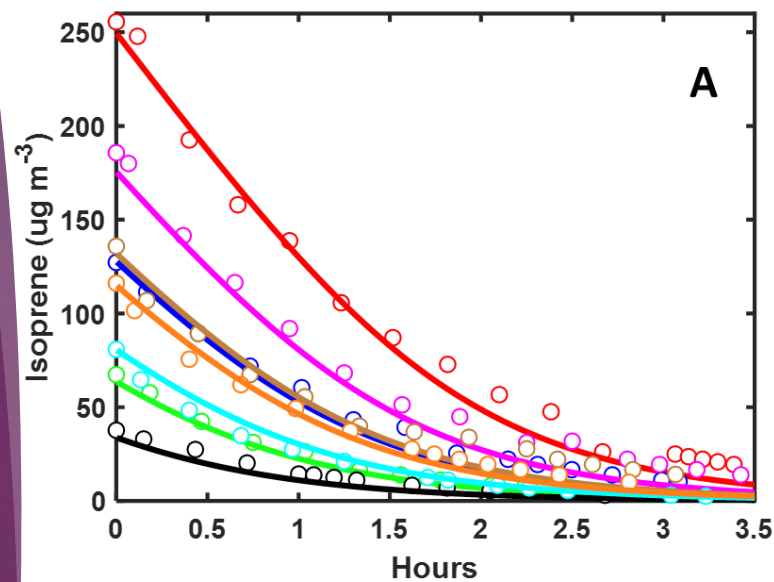
# Comparison to PNNL-2018 without-NO$_x$ Experiments
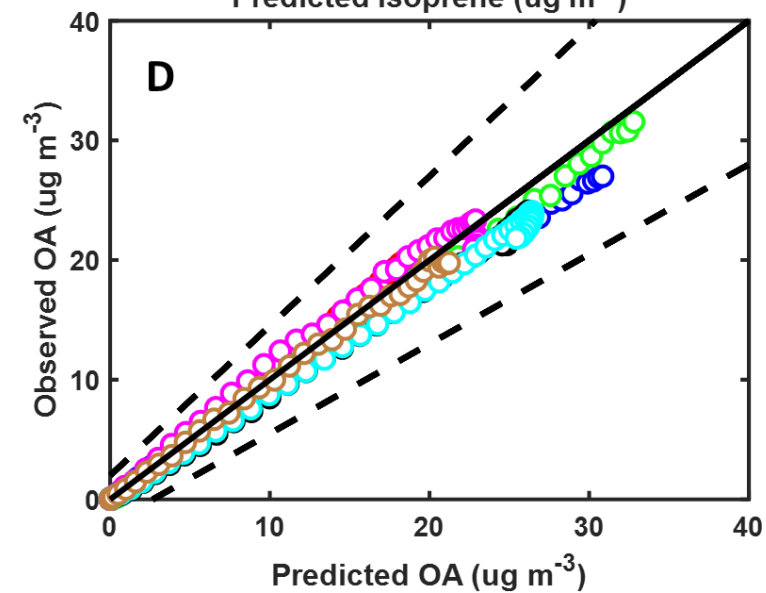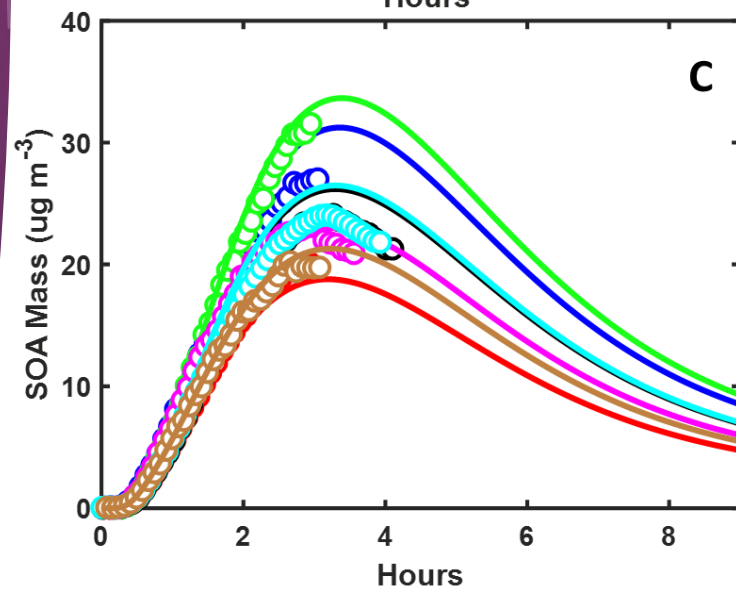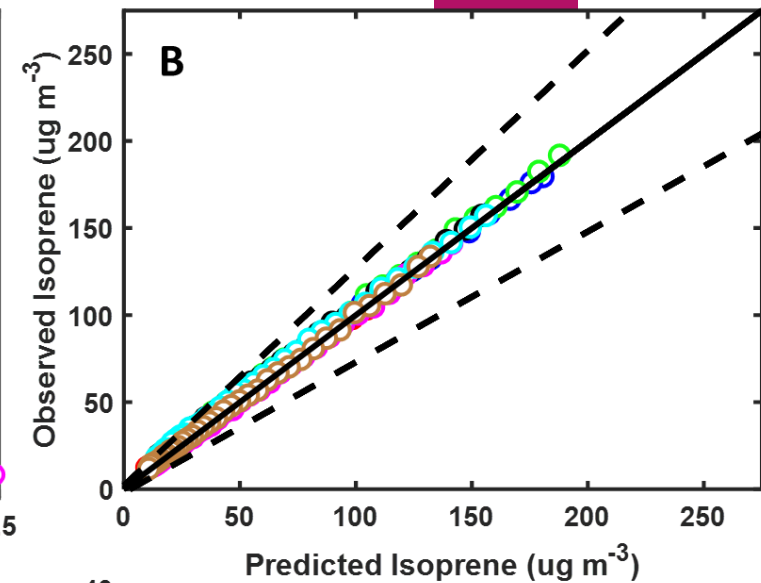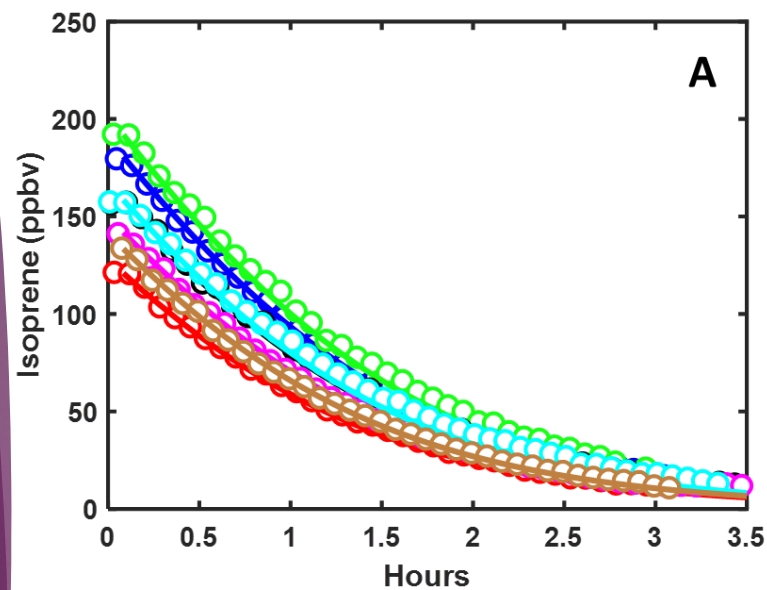
# Overall agreement w/in 25% for experiments without NO$_x$ added

- **Agreement similar for time-dependent and steady-stage experiments on different chambers by different groups 10 years apart**

- **Agreement requires:**
  - significant yield of second-generation ISOPOOH-derived peroxy radical (~20%): "DHHPO$_2$"
  - 1,5 H-shift of DHHPO$_2$ to yield hydroxy epoxide (0.4 s^{-1})
  - particle-phase photolysis of –OOH containing components (~0.02*j$_{NO2}$)
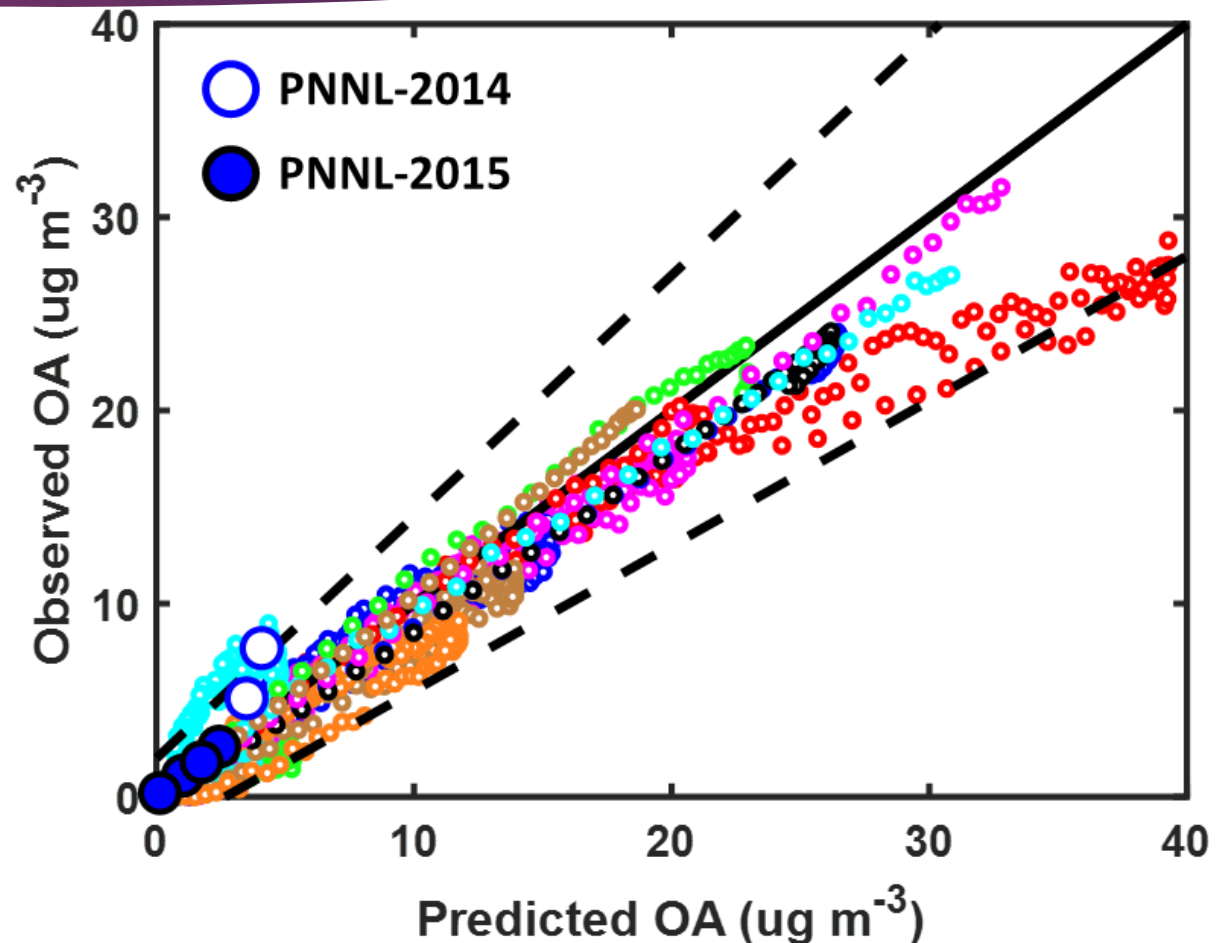
Extrapolating to the atmosphere

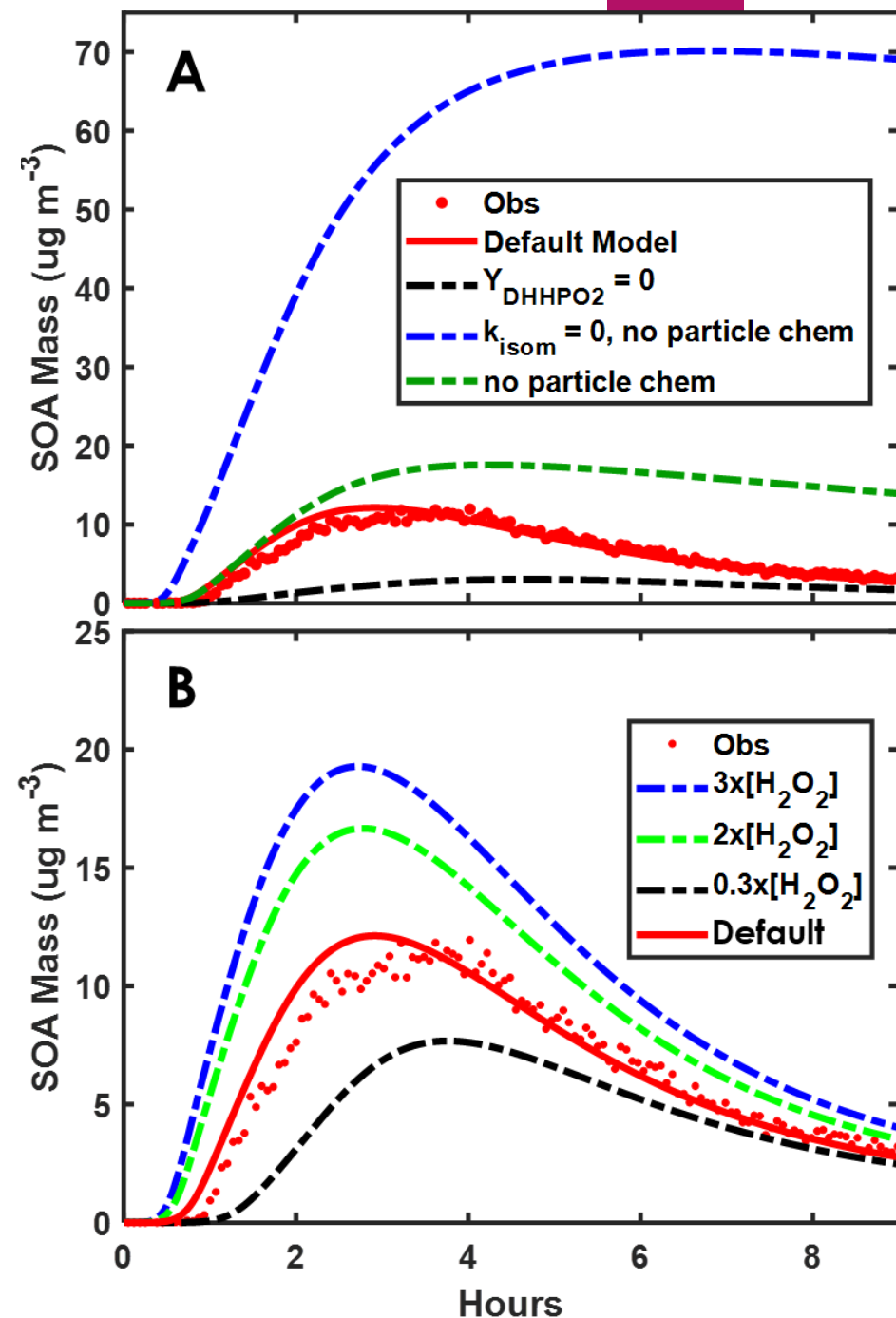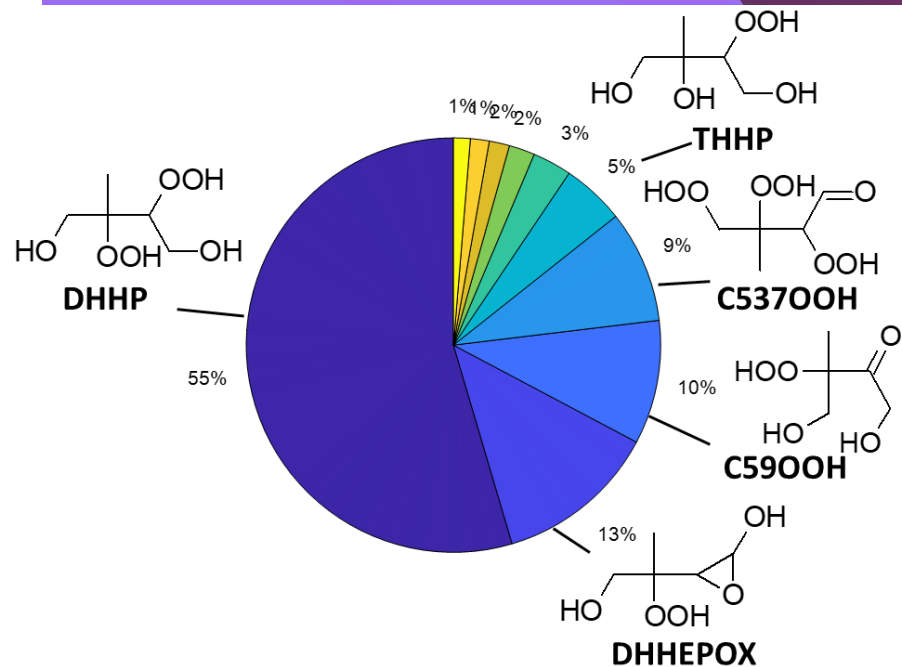**Model and experimental uncertainties**
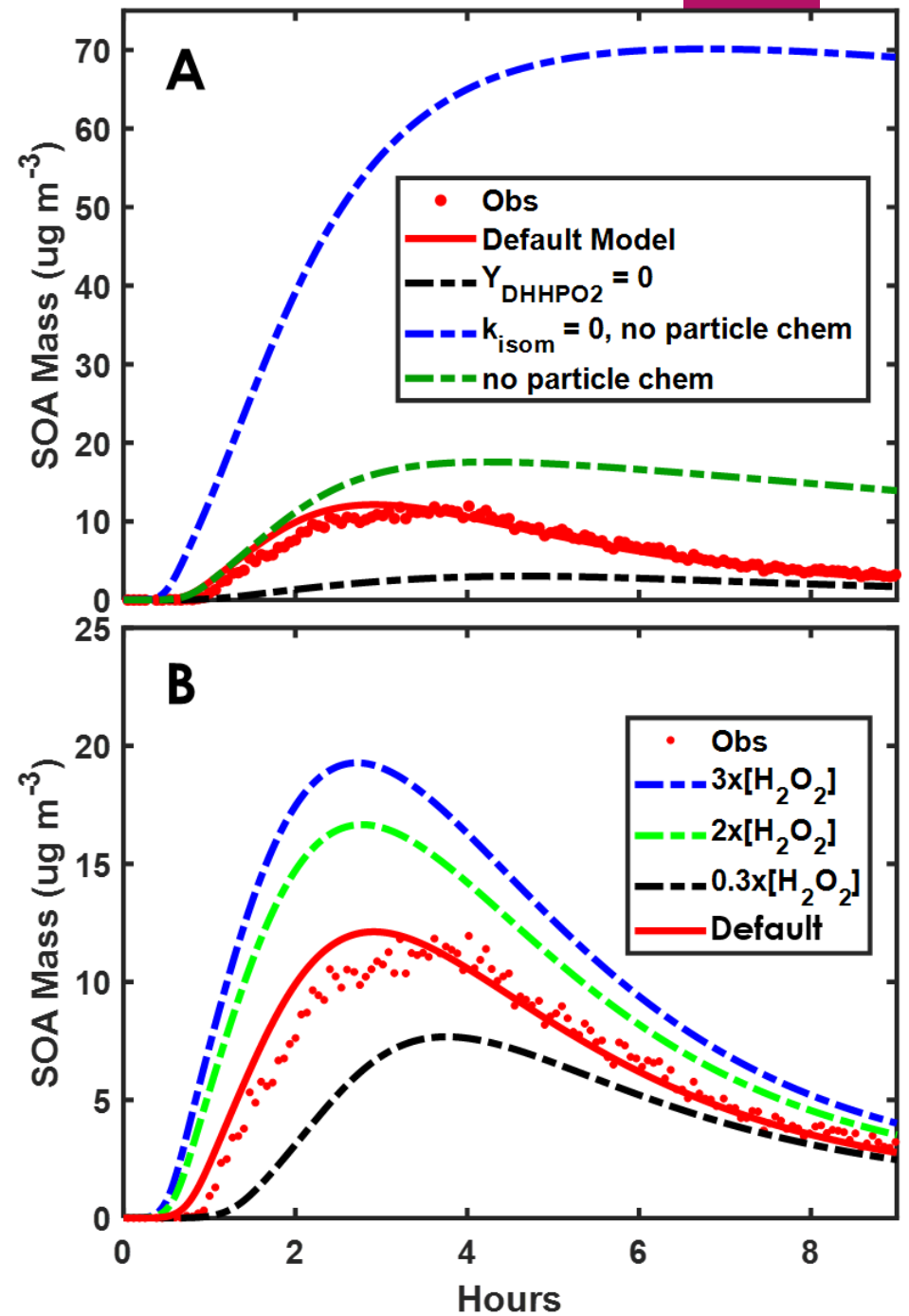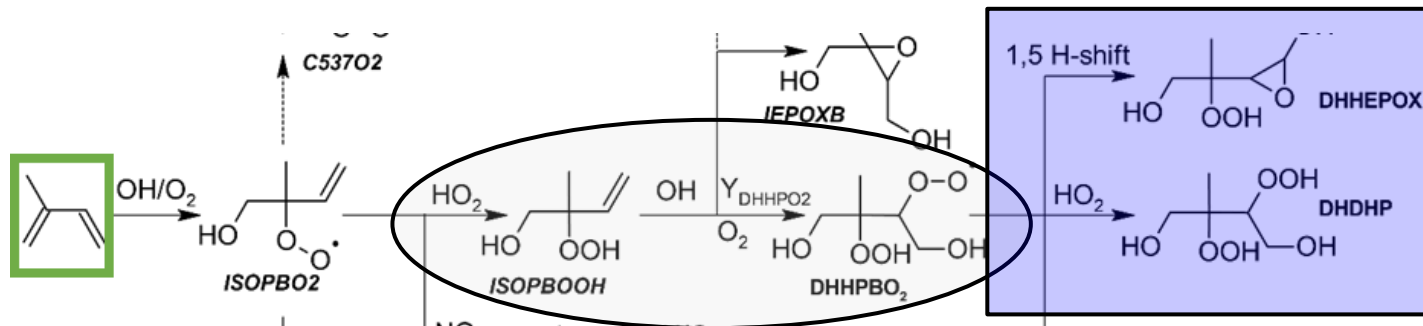
Extrapolating to the atmosphere

<u>Chemical parameters</u>

❑ Y_{DHHPO2} **needs to explain observed DHDHP content**

❑ **1,5 H-shift needed to explain H_2O_2 dependence**

❑ **1,5 H-shift rate constant from theory ~ 0.8 s^{-1} with ~factor of 5 uncertainty**
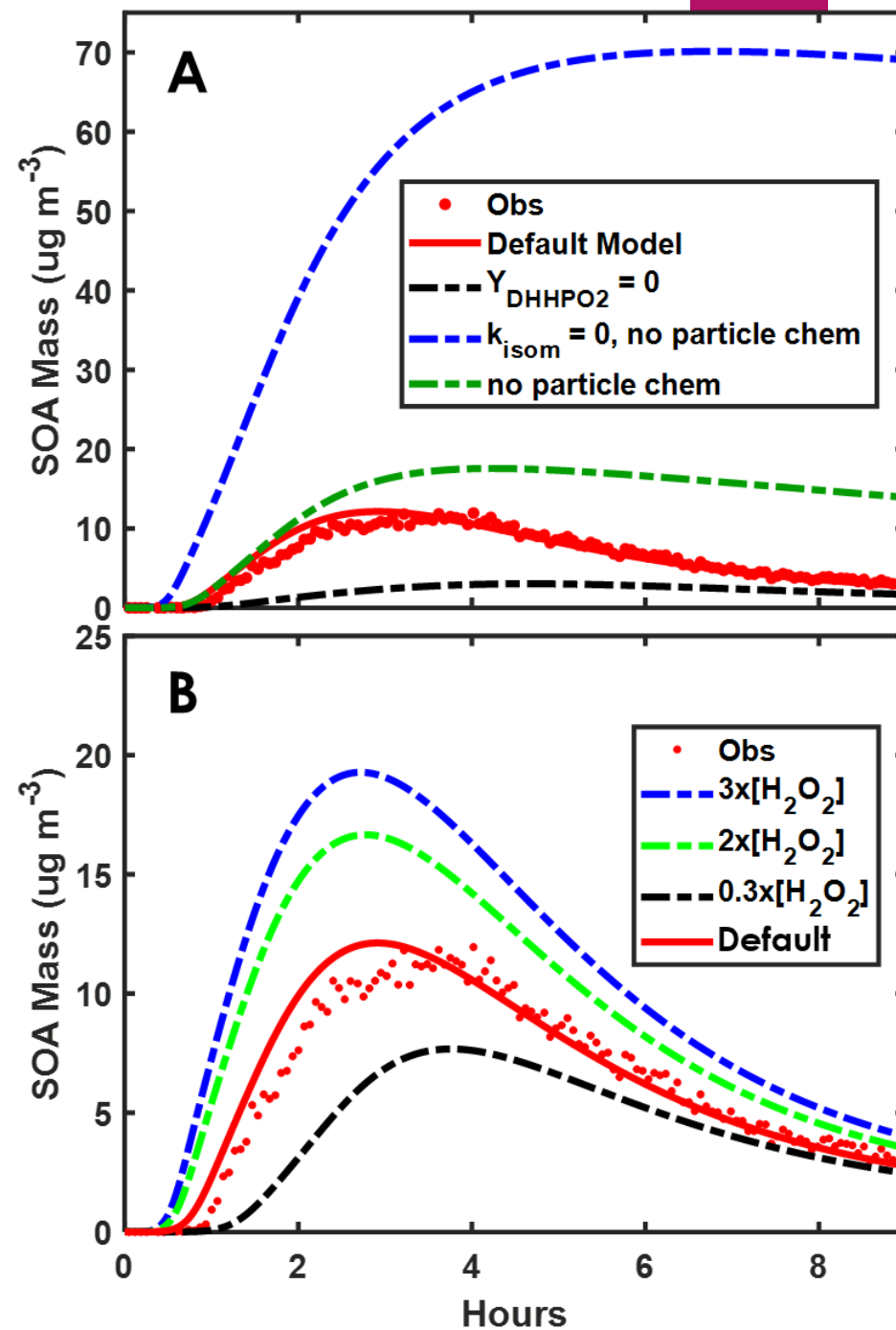
❑ **D'Ambro ES&T 2017; Møller et al JPC 2019**

Extrapolating to the atmosphere

Chemical parameters

Particle-phase -OOH photolysis required

DHHP 55%

DHHEPOX 13%

C59OOH 10%

C537OOH 9%

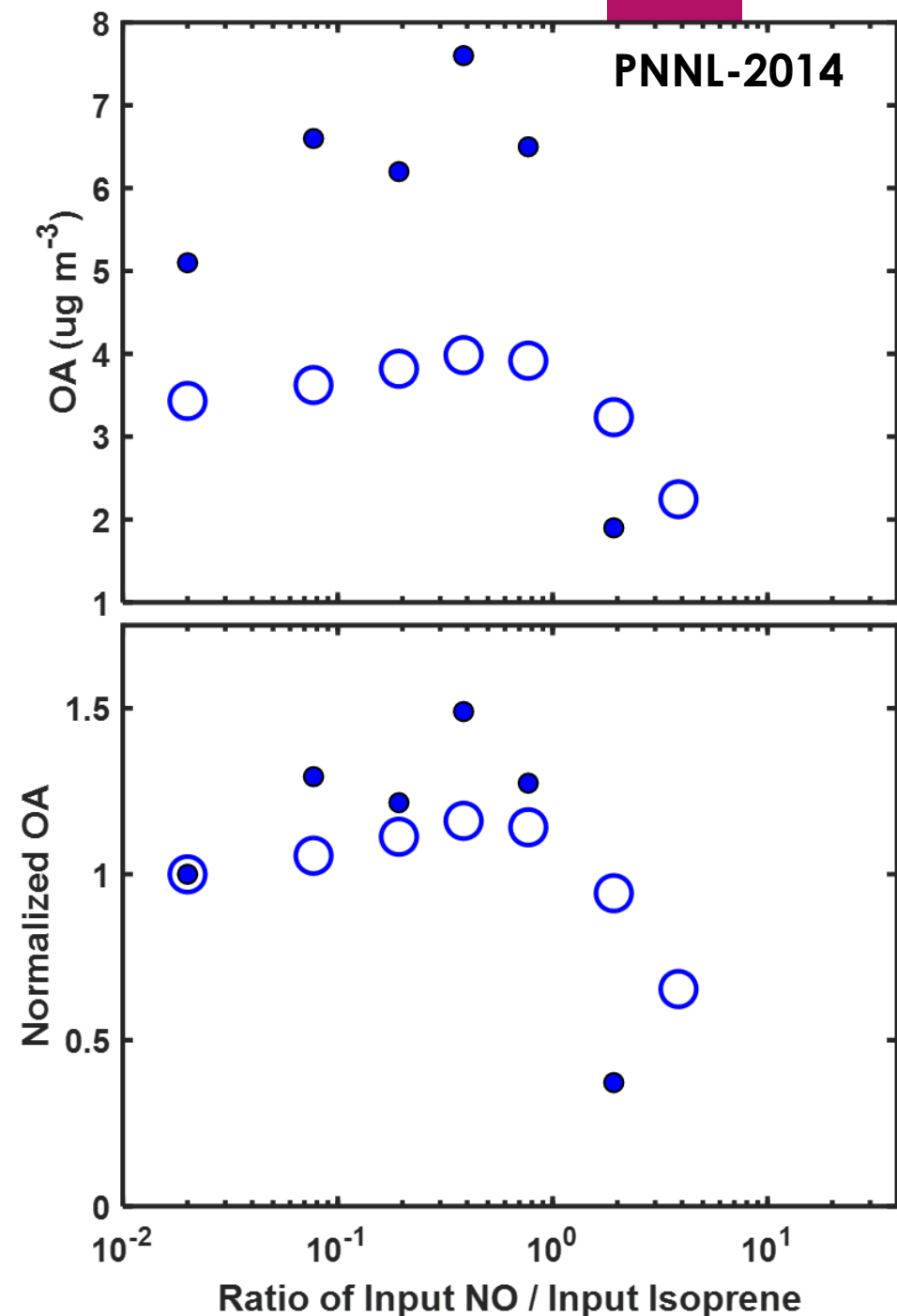THHP 5%

3%

2% 2% 1% 1% 1%

Extrapolating to the atmosphere

Role of NO$_x$:

SOA response to NO partly captured by model for continuous-flow experiments

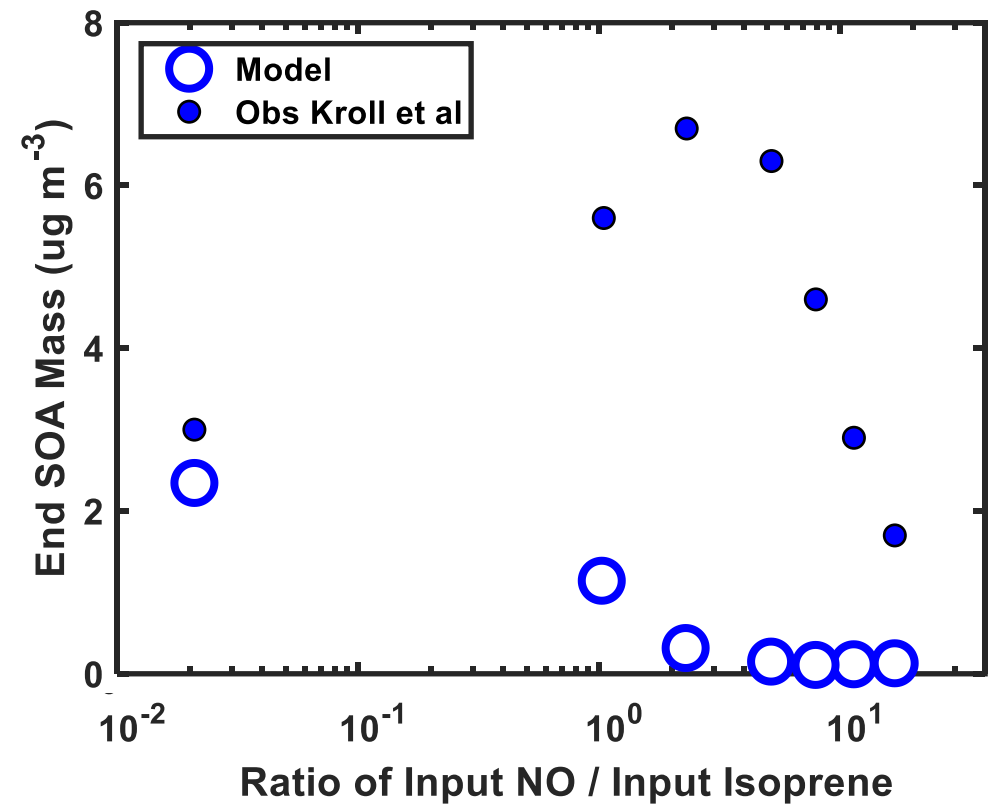**Some issues likely related to NO$_x$-HO$_x$ interactions and recycling**

PNNL-2014

Extrapolating to the atmosphere

Role of NO_x

SOA response not at all captured by model for time-dependent experiments

Extrapolating to the atmosphere

Role of NO$_x$

SOA response not at all captured by model for time-dependent experiments

Potentially explained by second-generation organic nitrate *accretion reactions, but __NOT__ hydrolysis*
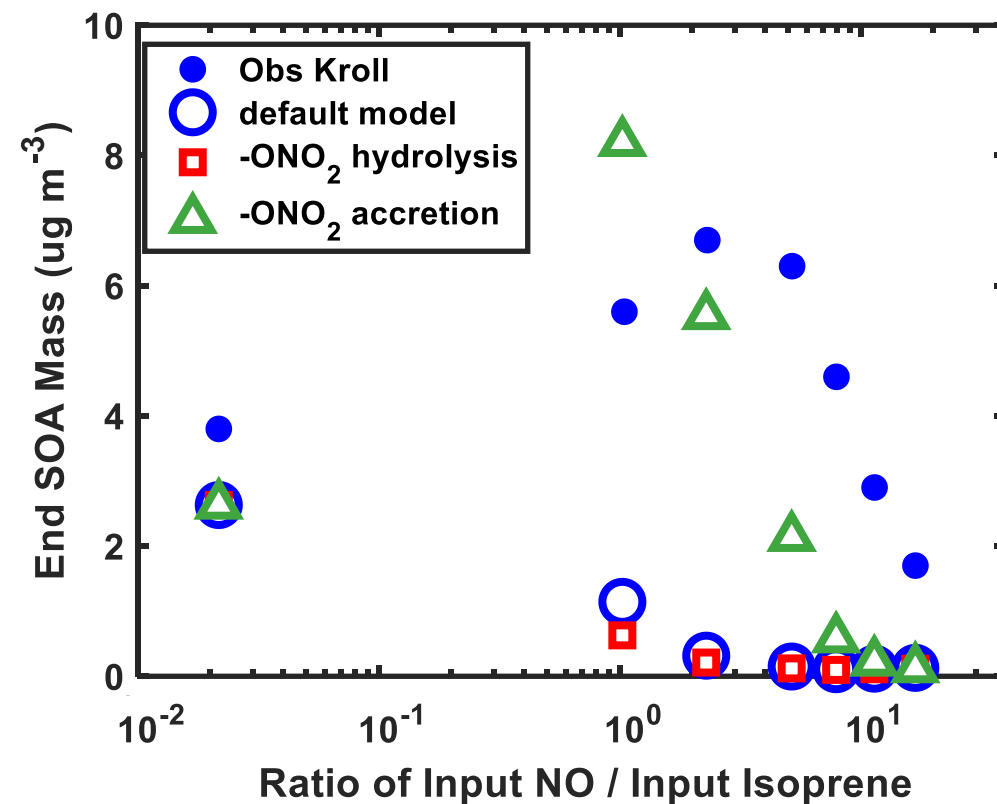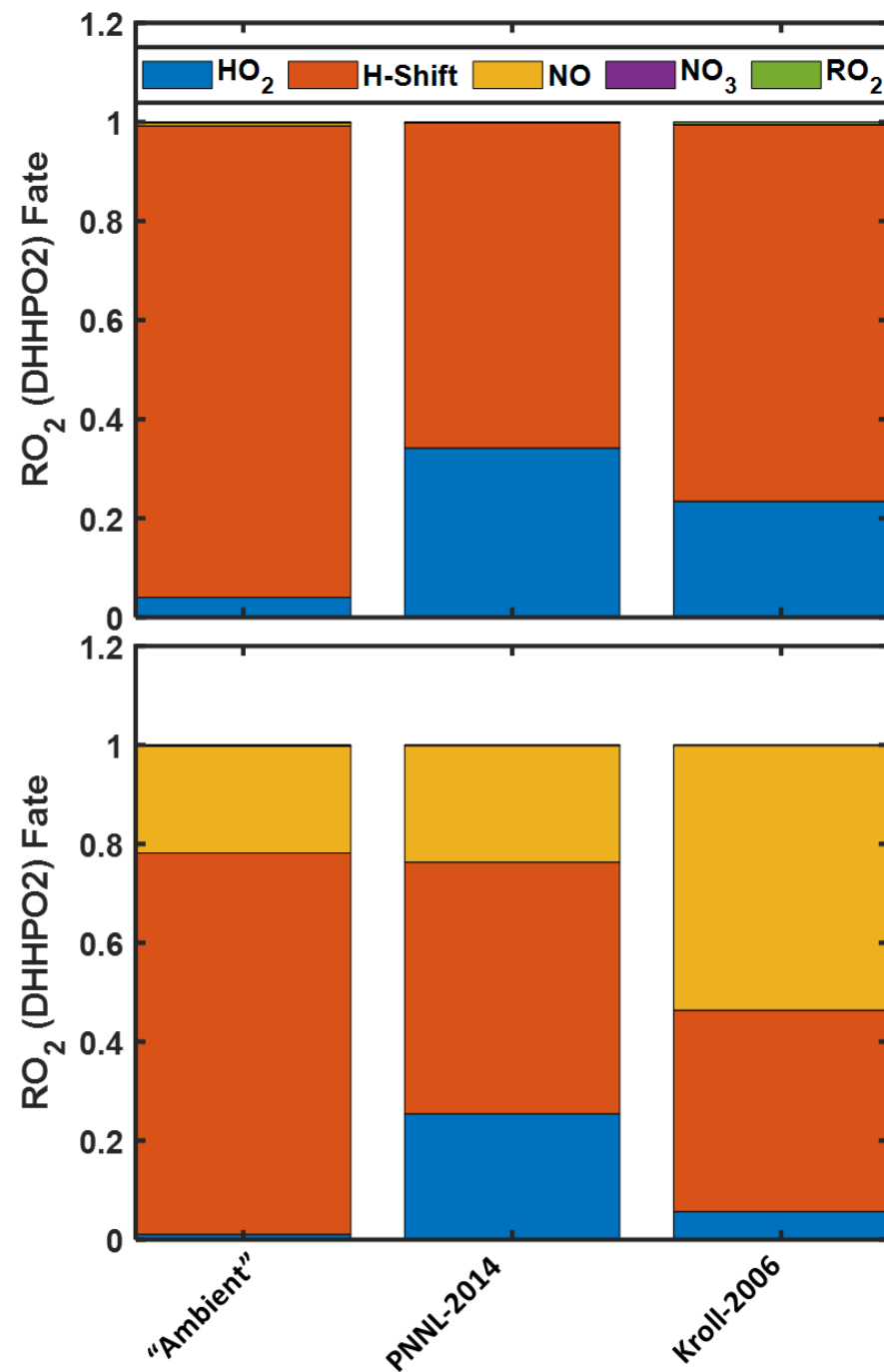
Extrapolating to the atmosphere

RO$_2$ Fate:

Fate of key RO$_2$ (DHHPO$_2$) in chambers is >10x skewed towards reaction with HO$_2$

Even with substantial NO$_x$ added

Role of unimolecular 1,5 H-shift far more important in the atmosphere

→ Implies significant T dependence
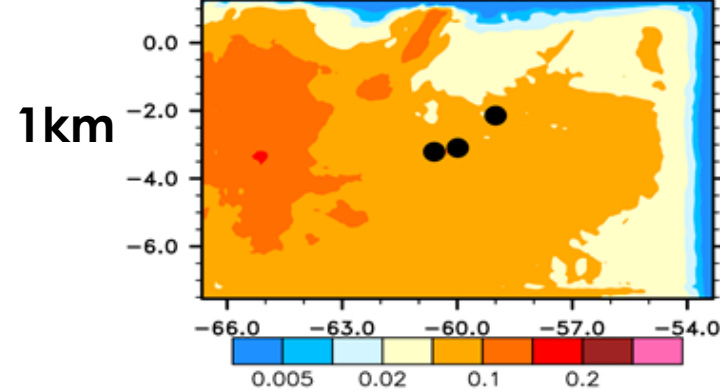

Without NO$_x$

With NO$_x$
(0.5 – 1 ppb NO)

Use mechanism to bound importance of volatility-driven Isoprene SOA

Box-Model for "Typical" Boundary Layer Conditions

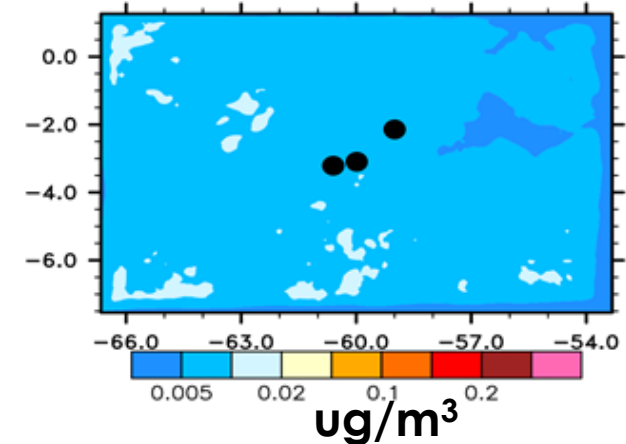Maximum Isoprene SOA Yield (%)
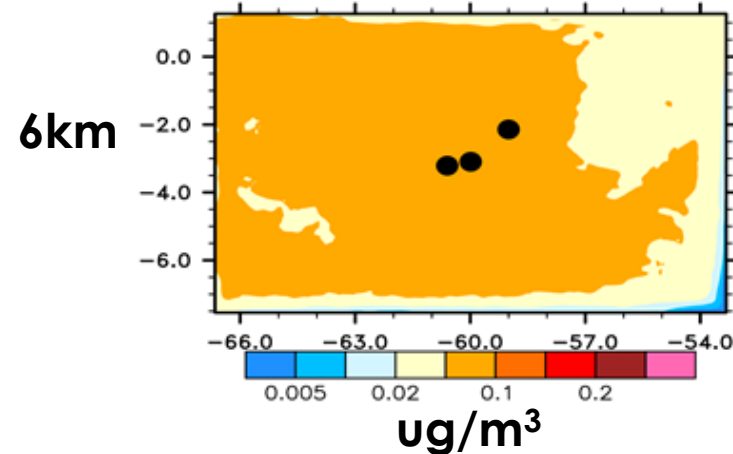
288K 10 ppt NO

500 ppt NO

298K 10 ppt NO

Pre-existing OA (ug m^{-3})
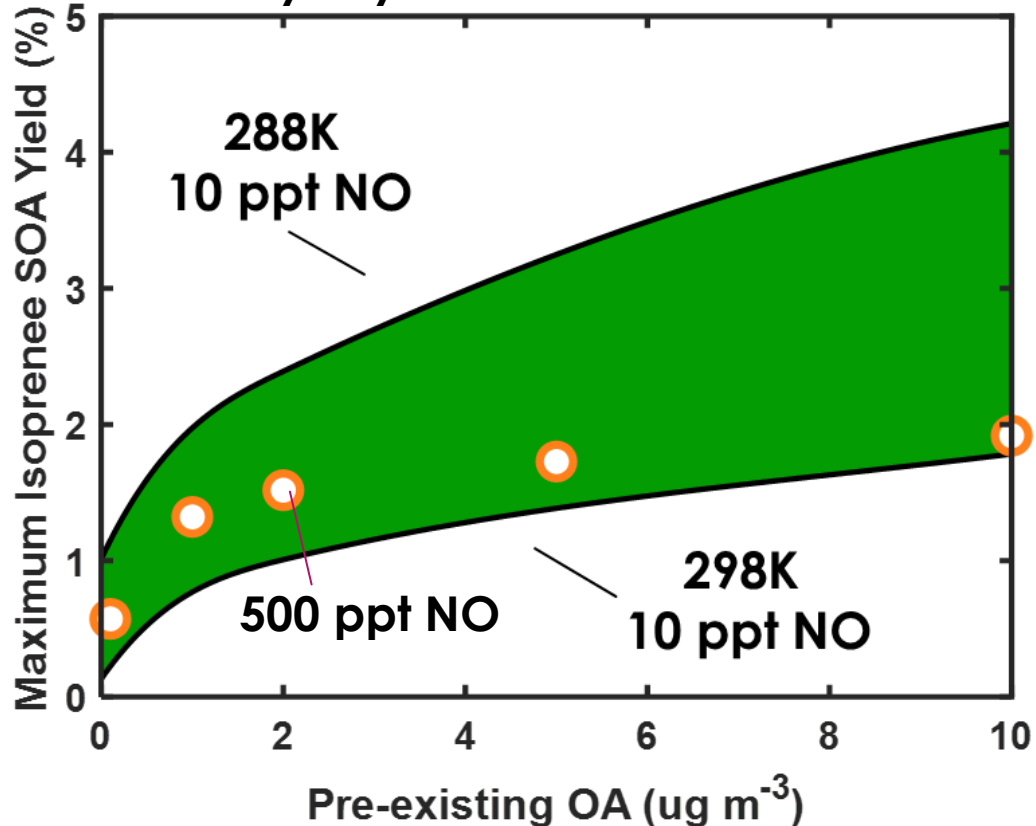
DHHPO$_2$ Pathway SOA

VBS Isoprene SOA

1km
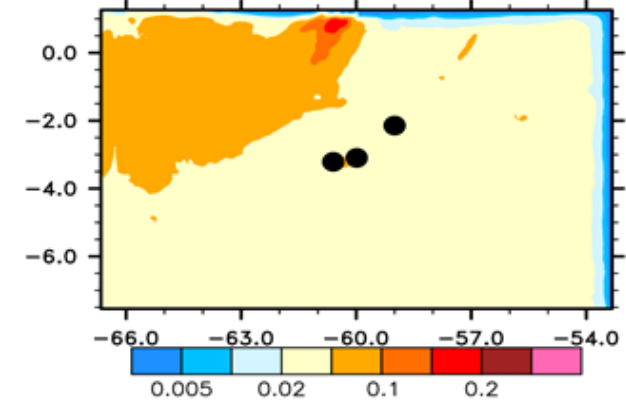
*WRF-Chem over Amazon near Manaus*

6km

ug/m^3

ug/m^3

Conclusions

- Near explicit mechanisms of isoprene low-NO_x oxidation can reproduce chamber generated SOA abundance and time evolution without assuming volatility distributions. Not so for experiments with NO_x

- RO_2 from ISOPOOH and its unimolecular 1,5 H-Shift play key role in setting volatility-driven SOA from isoprene with and without NO_x

- RO_2 fate in chambers highly perturbed from atmospheric conditions, demanding use of a mechanistic model with RO_2 H=Shift chemistry to extrapolate chamber yields to the atmosphere

- Relatively simple, mechanistic models of low-NO_x isoprene volatility-driven SOA are possible that will better capture the sensitivity to NO_x and temperature than common VBS approaches
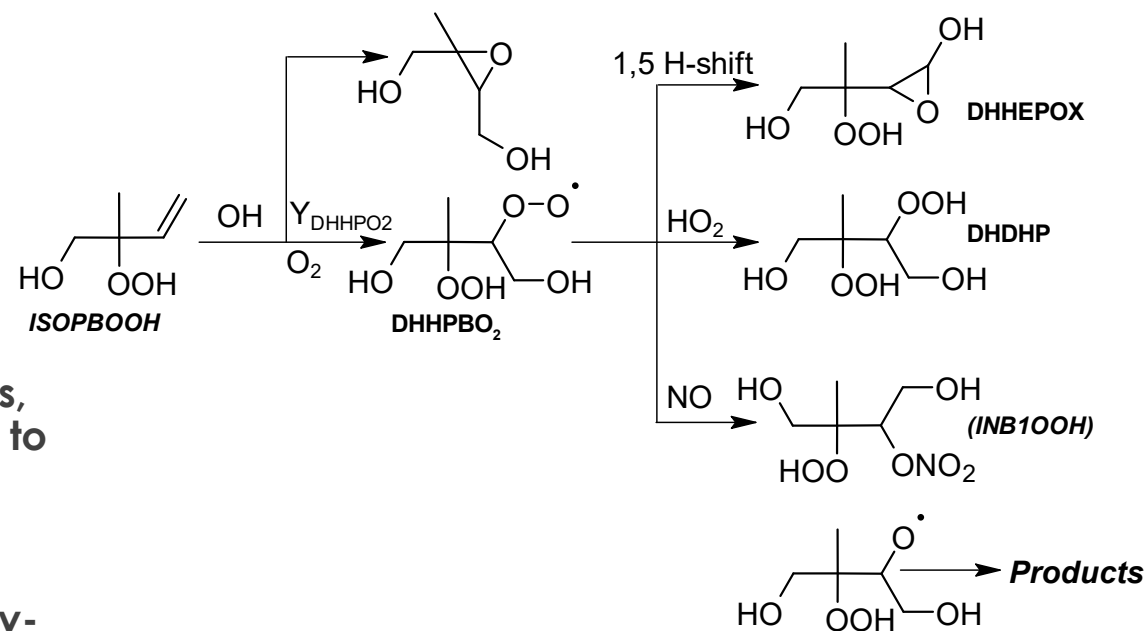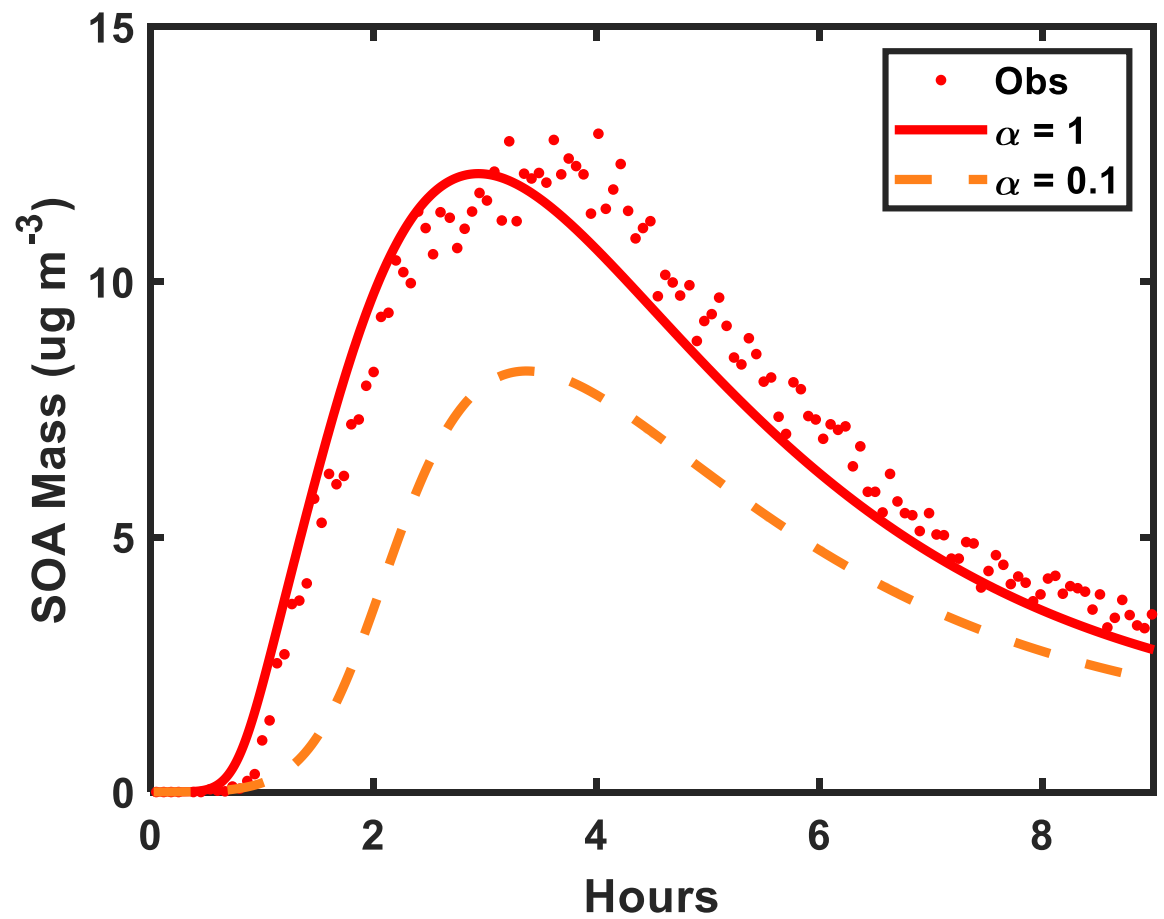
Vapor-wall loss effects

Including vapor-wall loss leads to lower SOA predicted.

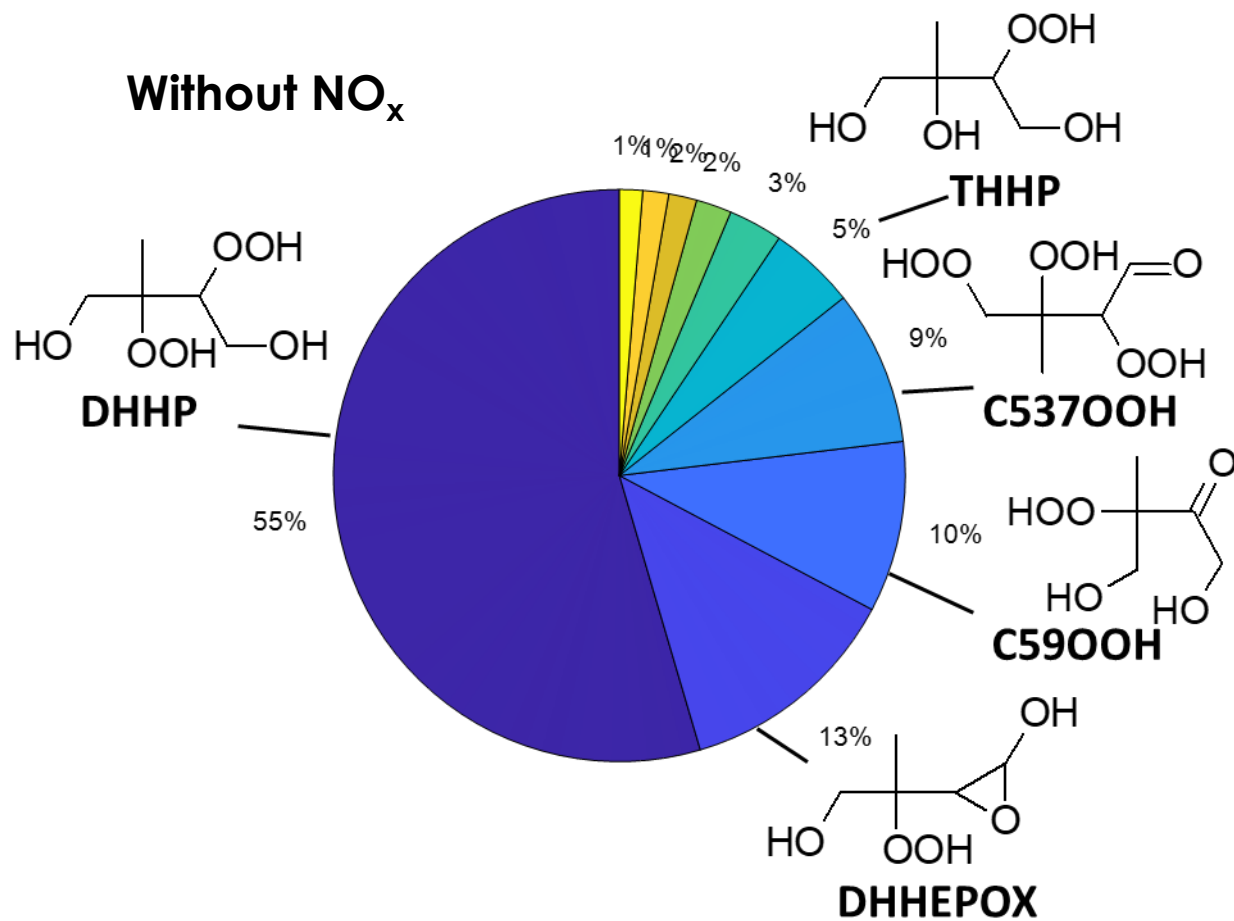**Uncertainty in 1 parameter, 1,5 H-Shift of key RO_2, is able to easily compensate for effect of vapor wall loss.**
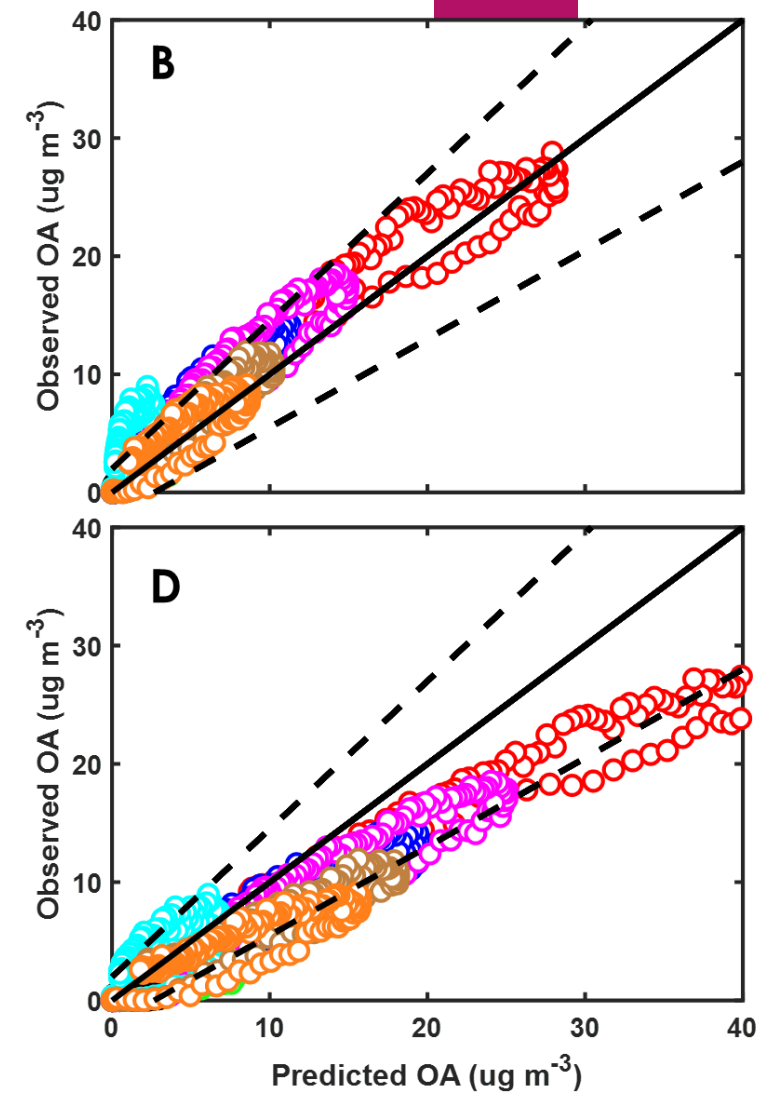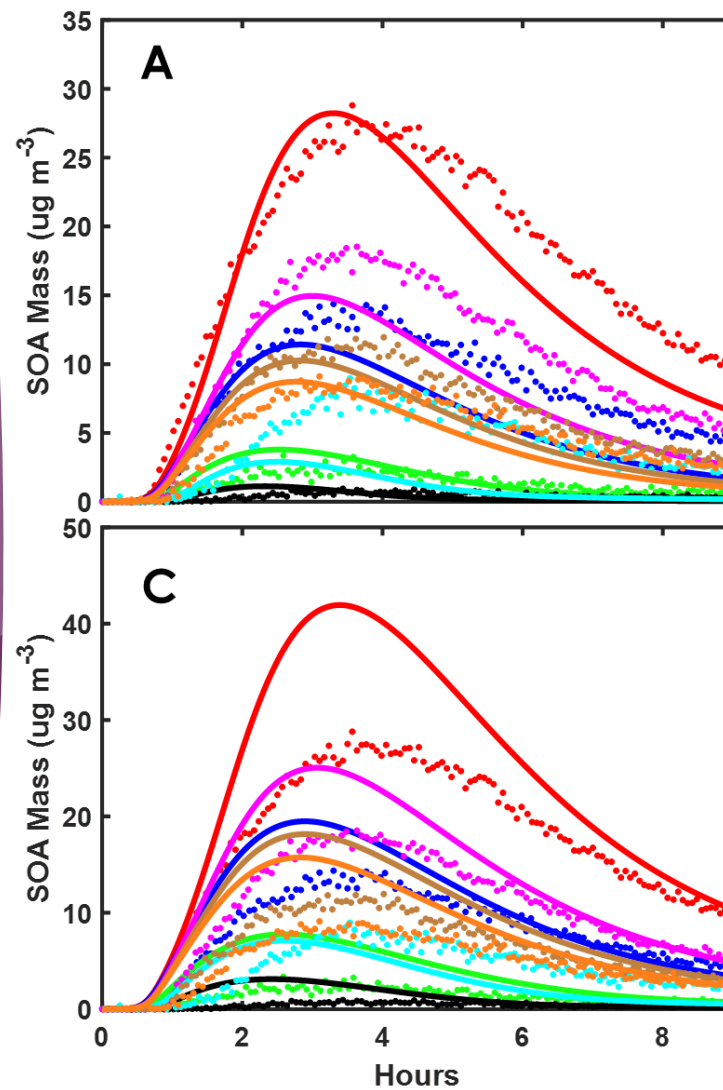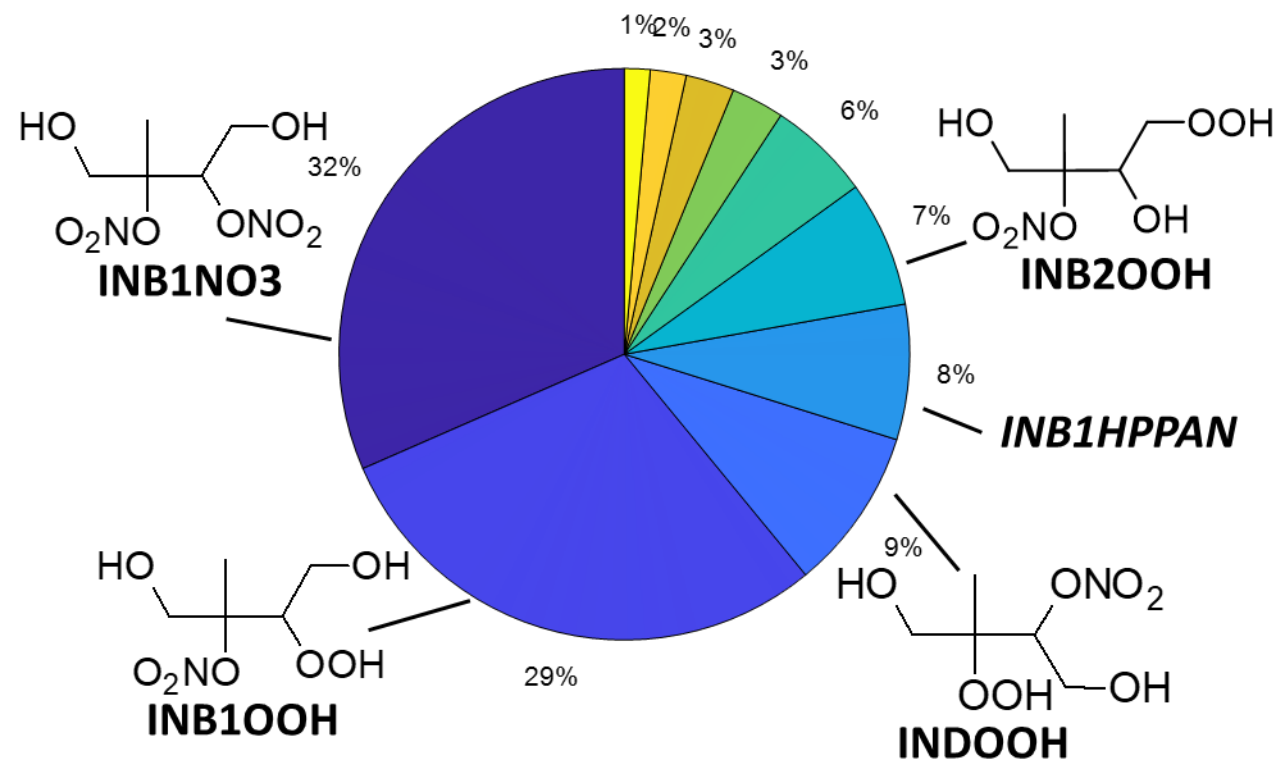
Mass accommodation

Predicted SOA Composition (Kroll-2006)

Kroll-2006 O$_3$, NO, NO$_2$

Kroll et al ES&T 2006