American Association for Aerosol Research

AAAR

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Evaluation of Regional-Scale Model Parameters in the Prediction of Isoprene Epoxydiol (IEPOX)-Derived Secondary Organic Aerosols (SOA) Generated during Laboratory Chamber Experiments

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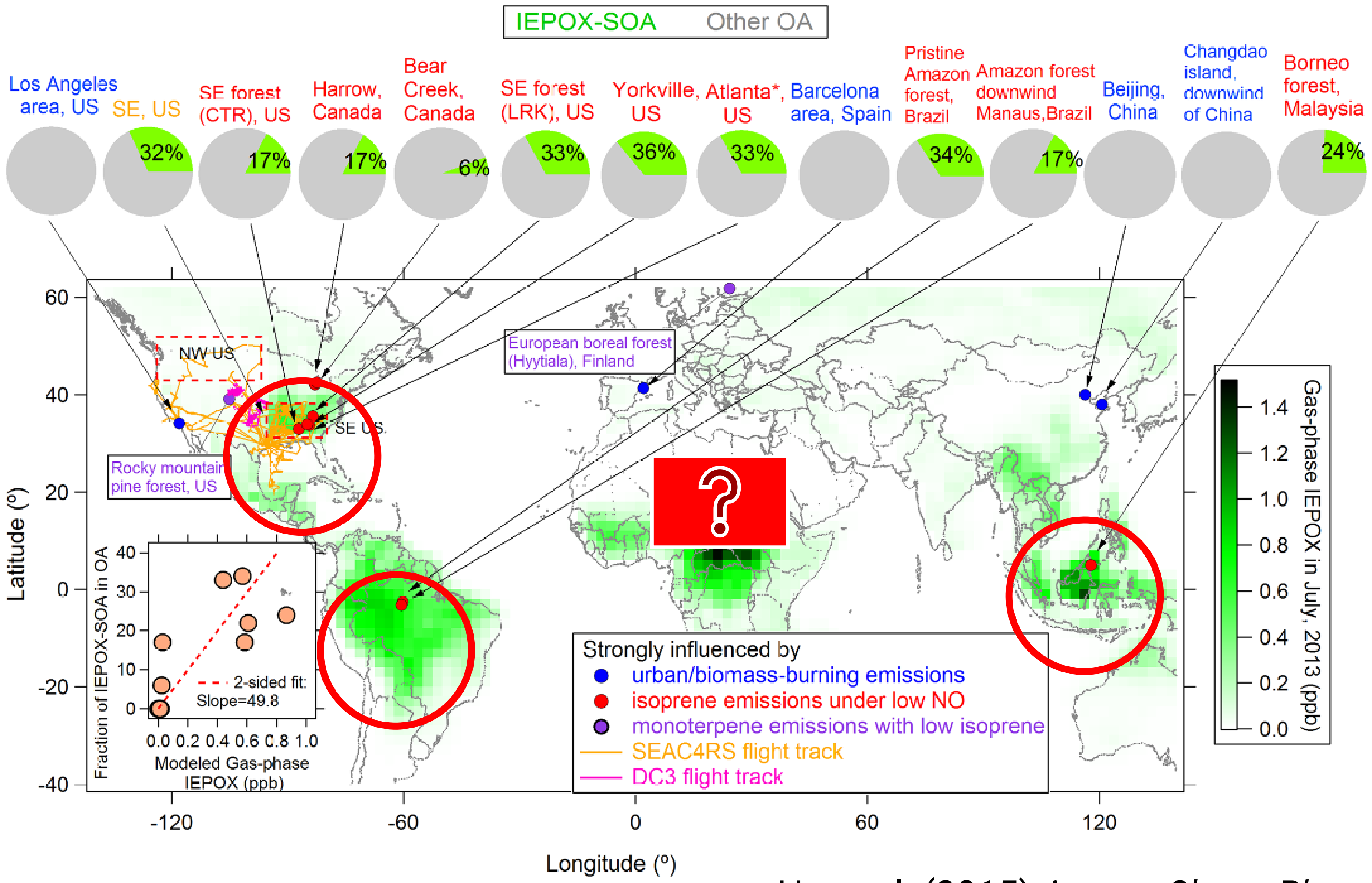
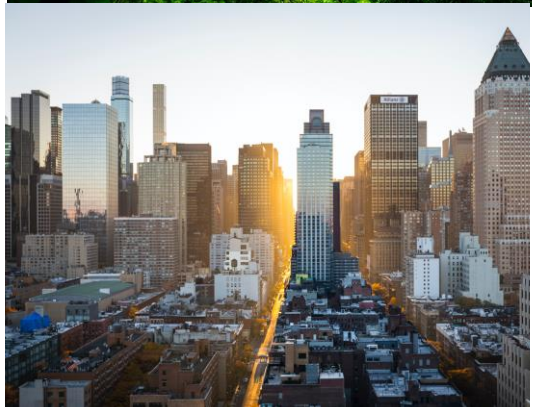
AAAR 2023

1. University of North Carolina at Chapel Hill, 2. Pacific Northwest National Laboratory, 3. University of California, Riverside

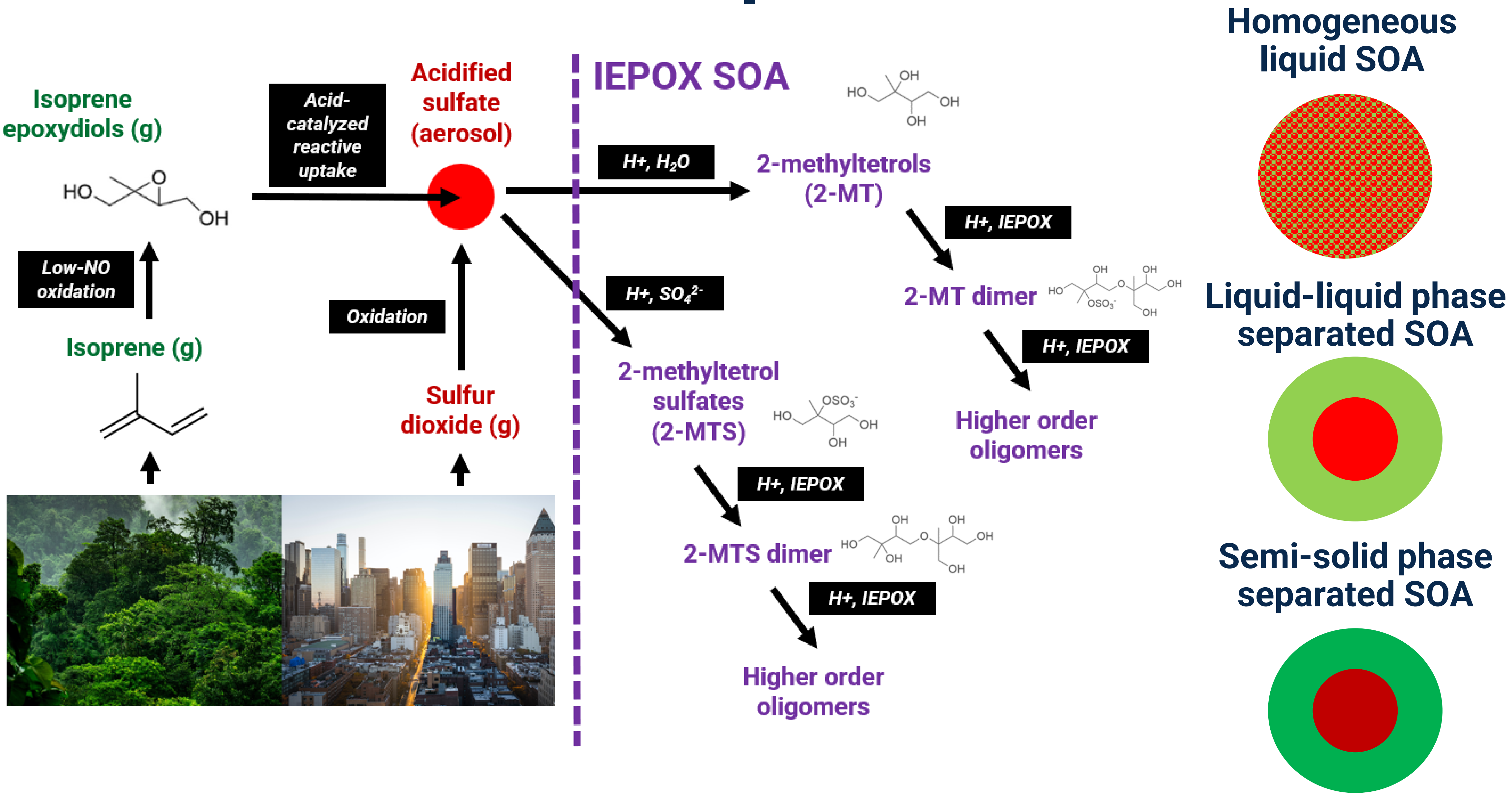
Isoprene epoxydiol (IEPOX) secondary organic aerosols (SOA) are formed at rural/urban interfaces



Hu et al. (2015) *Atmos. Chem. Phys.*



IEPOX SOA chemical processes



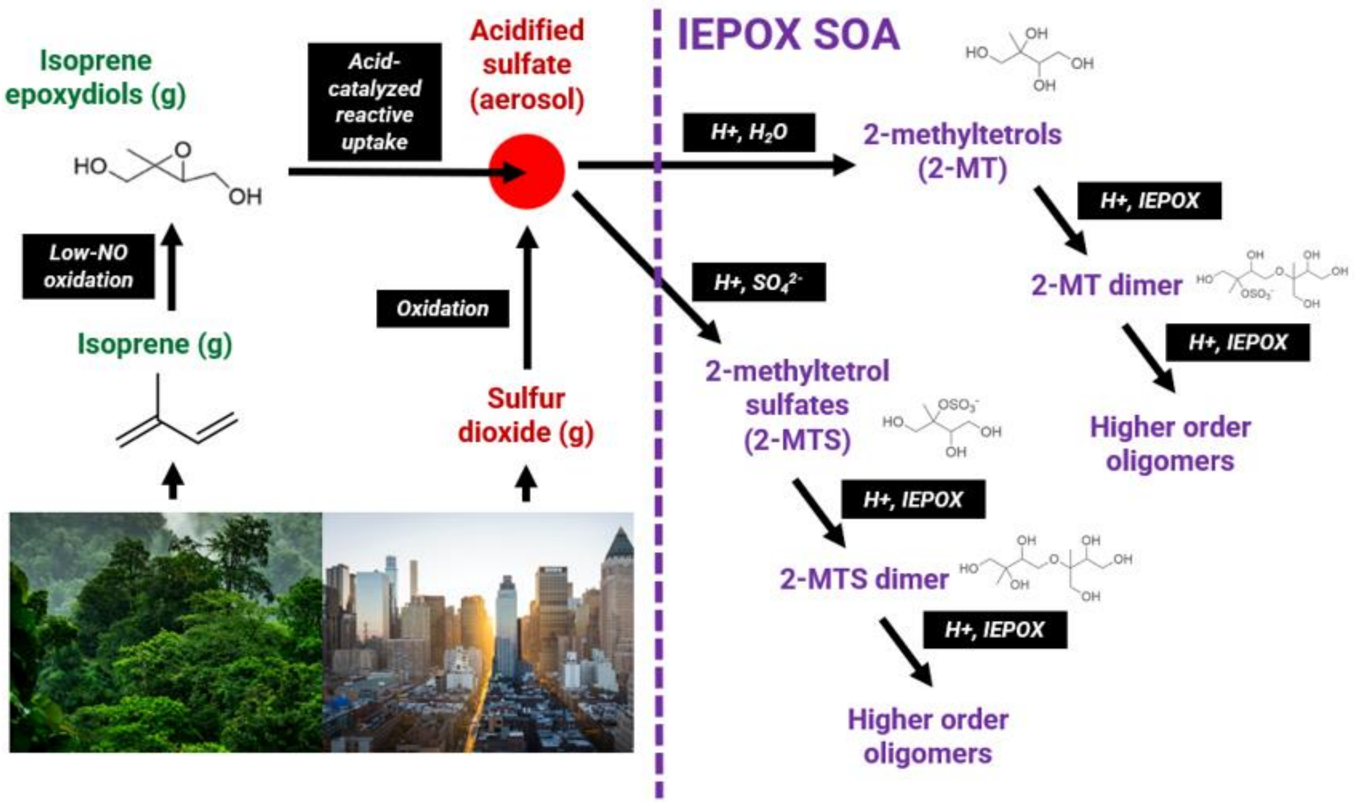
Modeling challenges

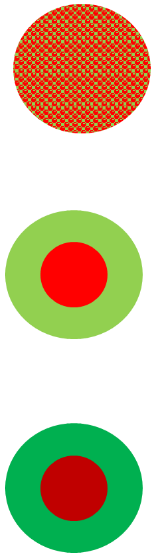
Critical physiochemical properties:

- Phase state/separation
- Acid-catalyzed reactive uptake
- Kinetics

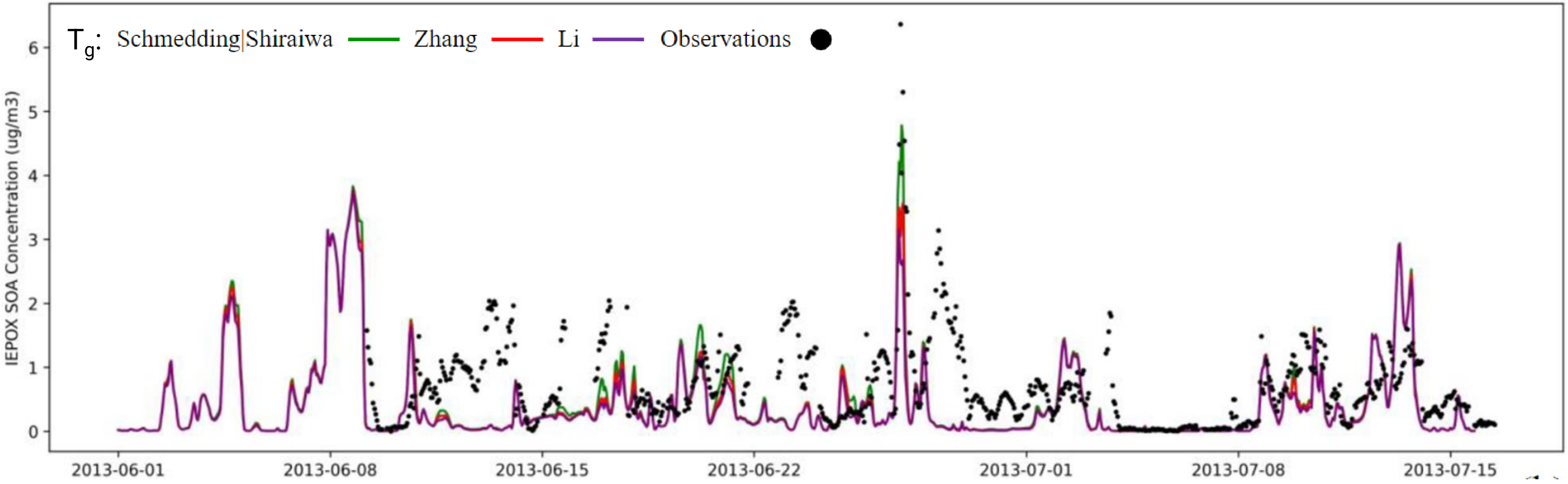
Environmental conditions:

- Relative humidity
- IEPOX:Sulfate ratios





Regional-scale models with phase separation underpredict IEPOX SOA



Farrell et al. Masters Thesis (2021) *University of North Carolina at Chapel Hill*
Farrell et al. (2023) *In prep*
Schmedding et al. (2020) *Atmos. Chem. and Physics*

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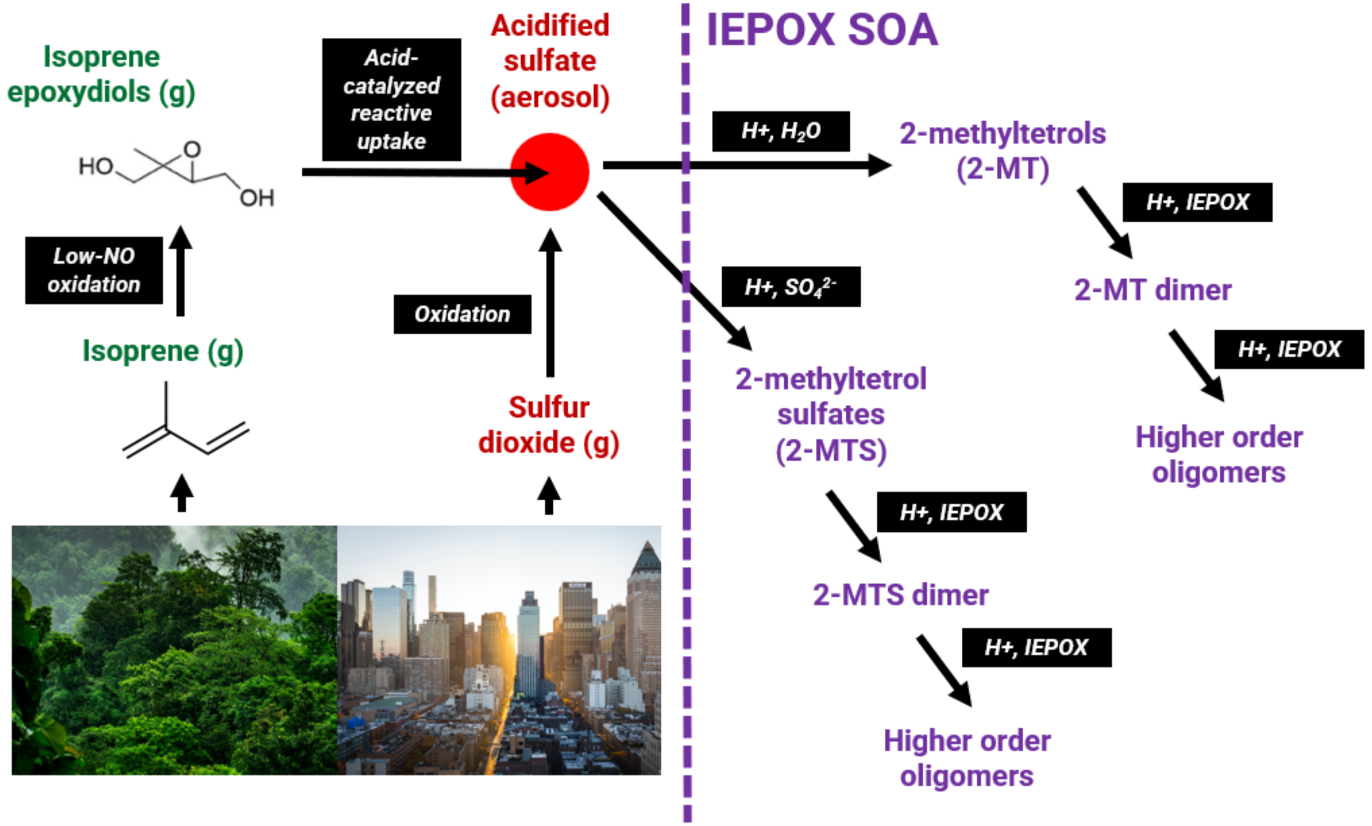
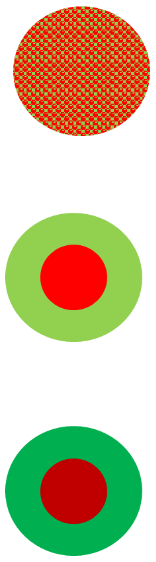
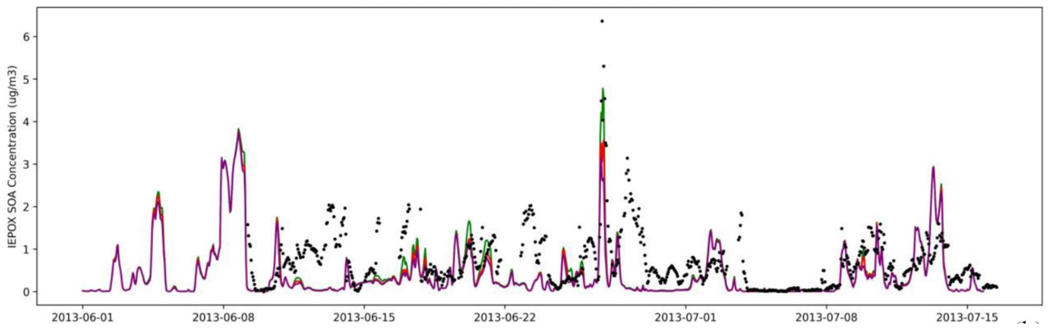
Remaining model uncertainties…

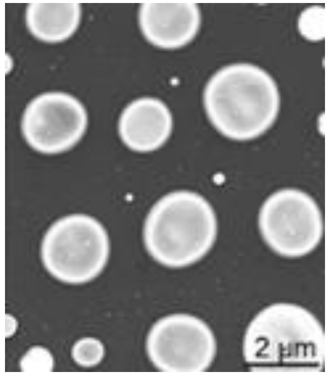
- Reactive uptake dependent on complex physiochemical properties and environmental conditions
- Organics not directly accounted for in regional-scale thermodynamic models for acidity
- Single heterogeneous rate constant controls total IEPOX SOA formed which is then fractioned into 2-MT, 2-MTS, and dimers

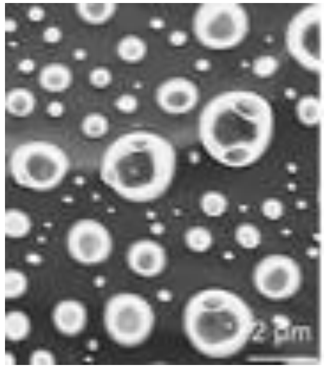






Connecting experimental findings with regional-scale modeling and application





1. What are the critical parameters in IEPOX SOA multiphase chemistry?
2. How can IEPOX SOA and other multiphase reactions be modeled more accurately and efficiently in regional-scale models?
3. What are the implications of this chemistry on rural/urban interaction in a changing environment?

Riva & Chen et al. (2019) *Environ. Sci. & Tech.*

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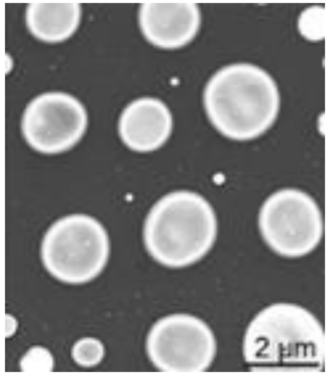

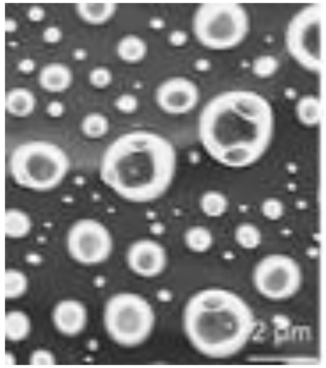

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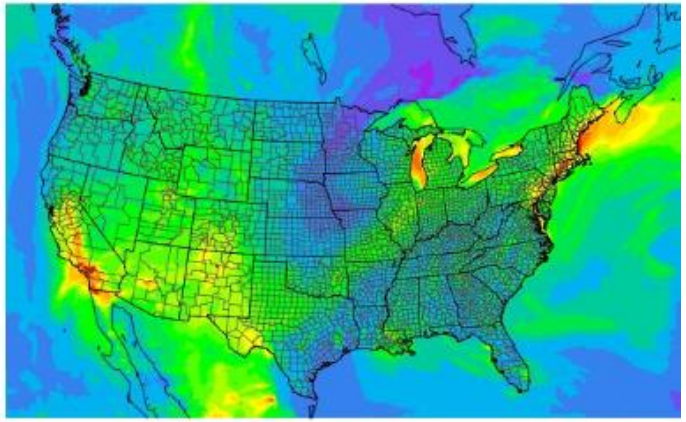

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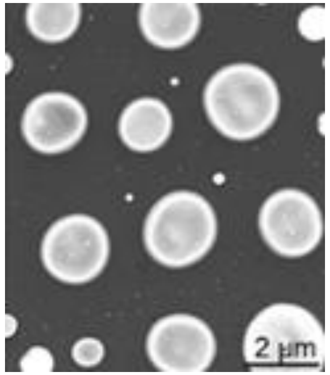

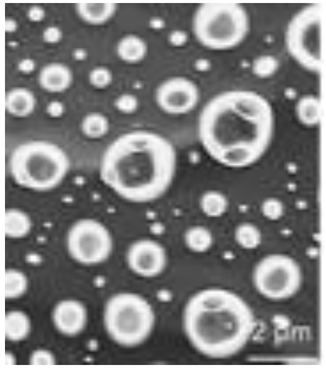

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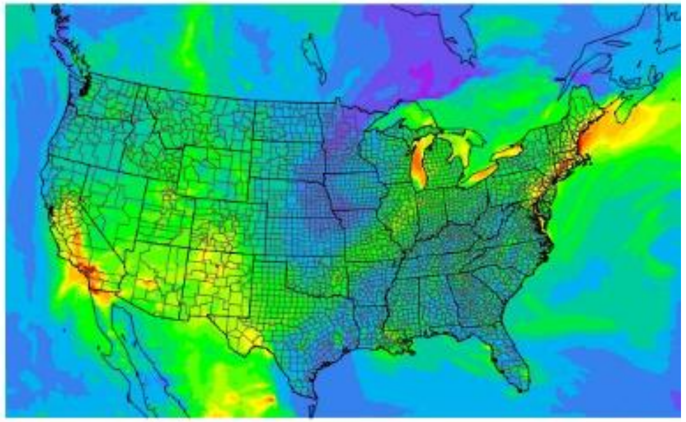
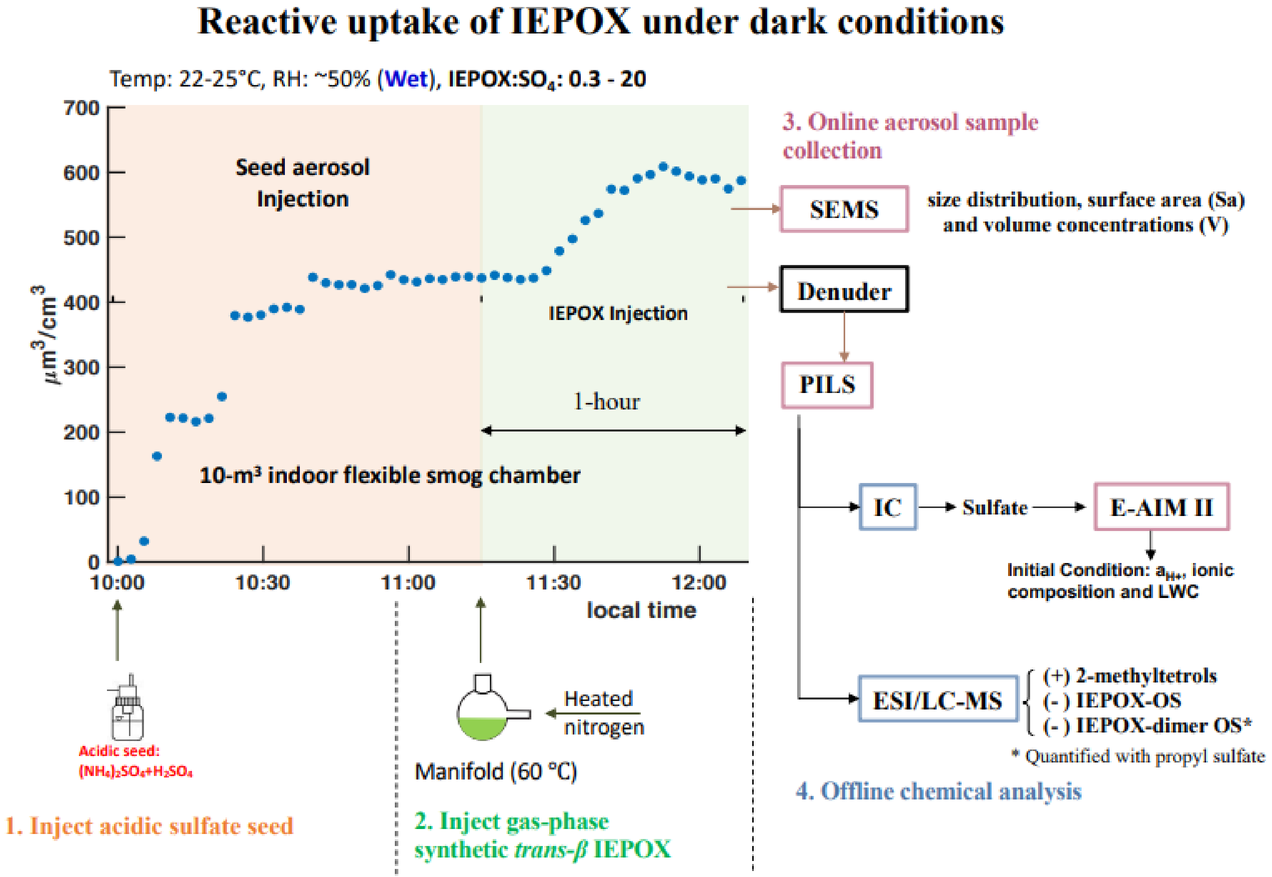


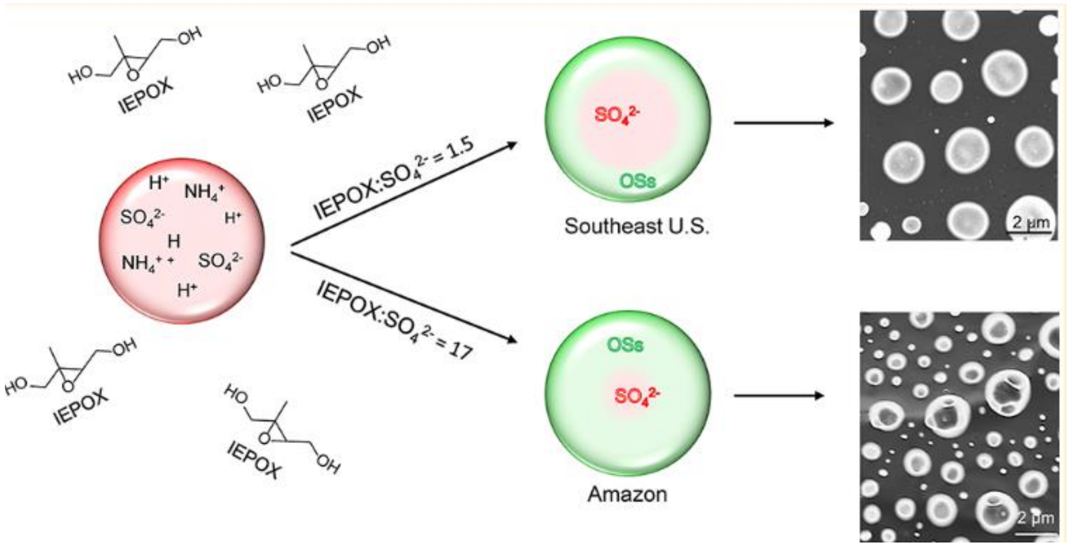
Riva & Chen et al. (2019) *Environ. Sci. & Tech.*

Methods

9 chamber experiments at variable IEPOX:Sulfate ratios in humid (50% RH) and dark conditions



Chen Thesis (2021) *UNC*



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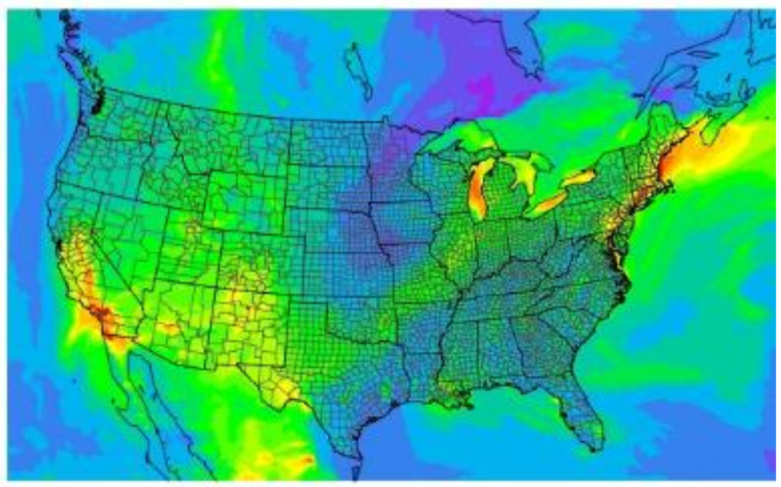
Modeling experiments with CMAQ aerosol modules

Community Multiscale Air Quality (CMAQ) Model

- Utilized and developed by the U.S. Environmental Protection Agency (EPA)
- Uses FORTRAN and is run on computing cluster
- Computationally expensive



3-D

Modeling experiments with CMAQ aerosol modules

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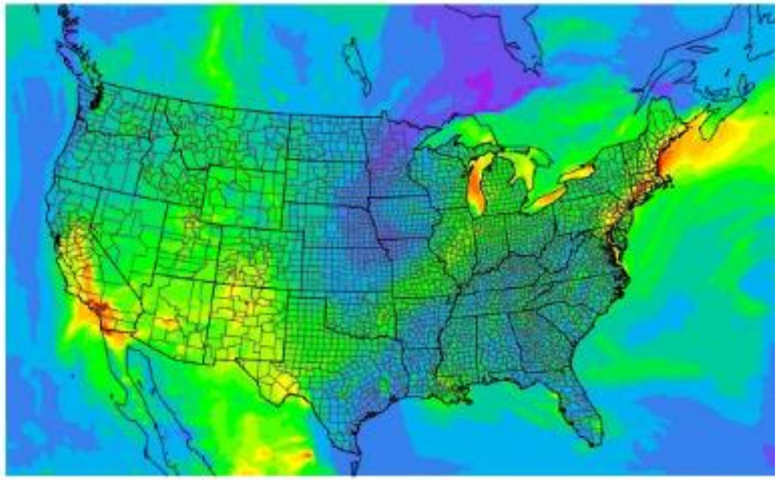
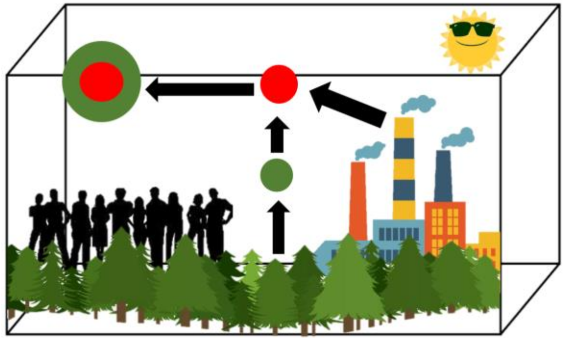
Chamber modeling with CMAQ modules in MATLAB

- CMAQ 5.3 modules translated to MATLAB by Jaime Green
- Can simulate CMAQ treatment of heterogeneous chemistry
- Computationally efficient for physiochemical parameter analysis



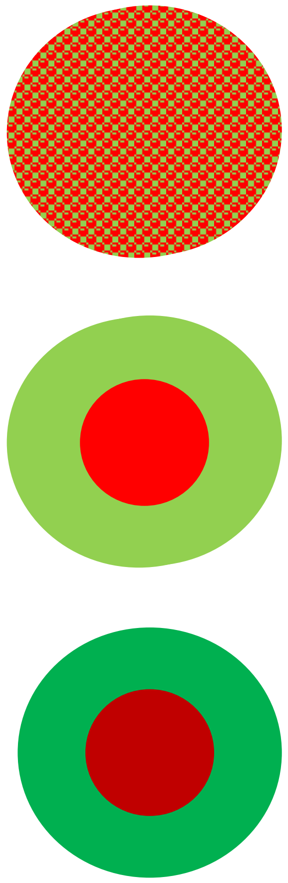
3-D



0-D

Modified CMAQ explicit multiphase chemistry model includes…

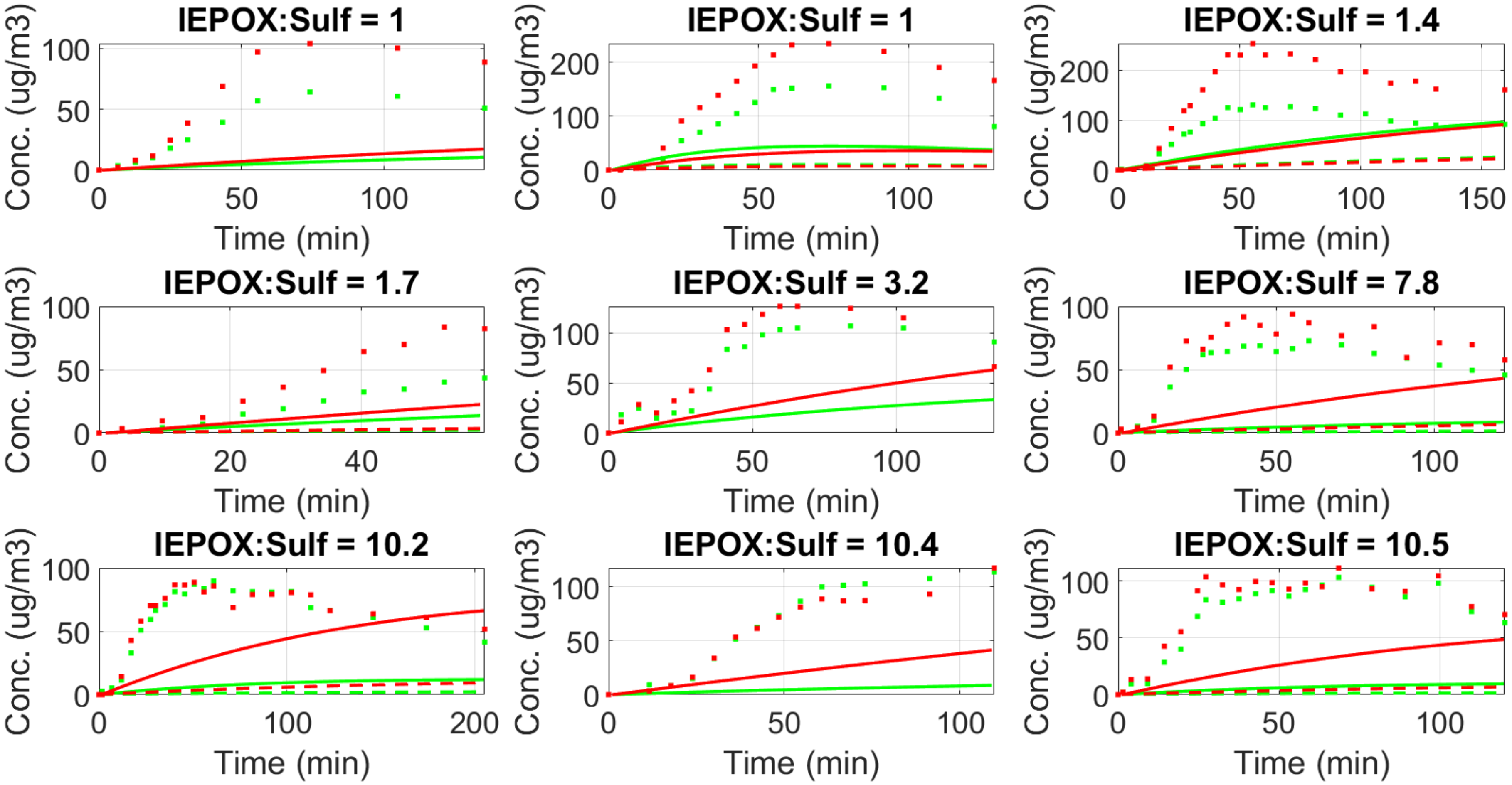
- **Phase state/separation prediction***
  - **Phase separated or homogeneous**
  - **Liquid or semi-solid organic shell**
- **Organic shell viscosity prediction**
- **Incorporates new scientific research on kinetics and reactive uptake**

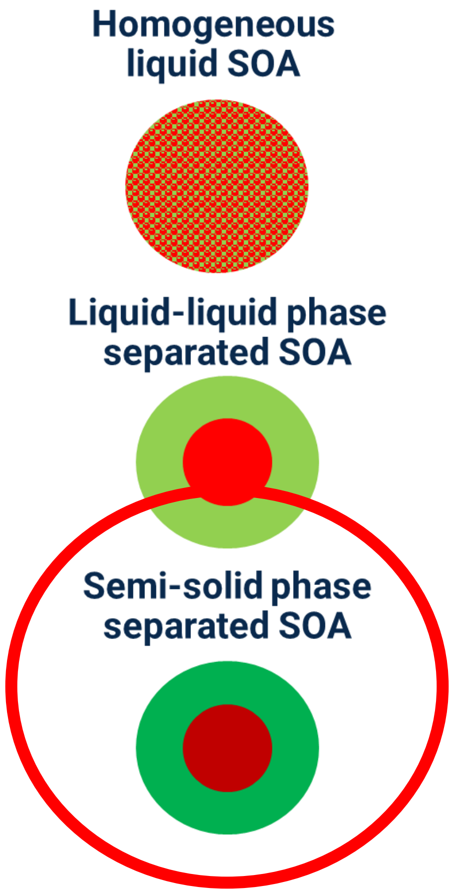


*Schmedding et al. (2020) *Atmos. Chem. and Physics*

Results

CMAQ homogeneous model underpredicted IEPOX SOA and phase separation model worsened predictions

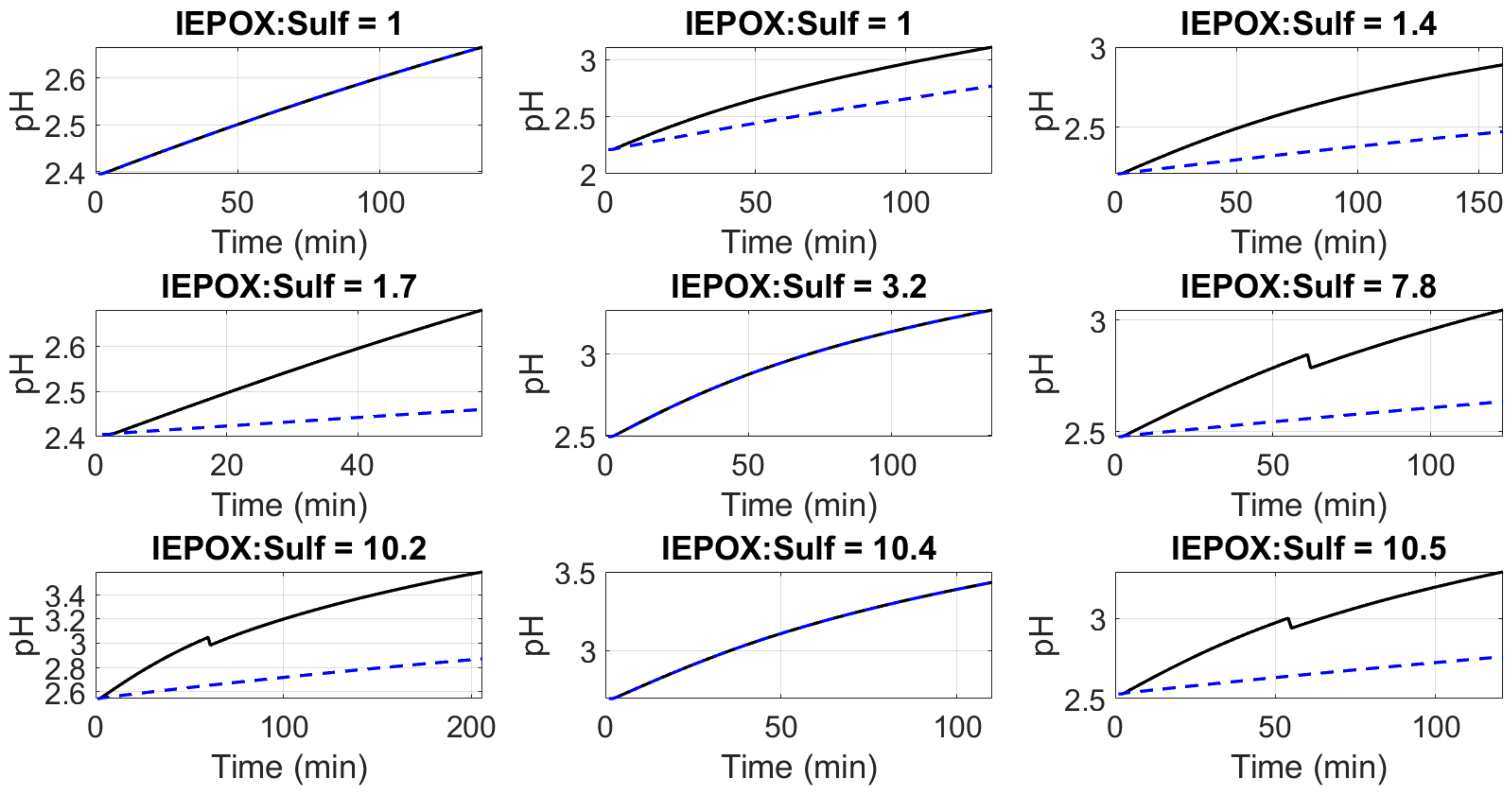


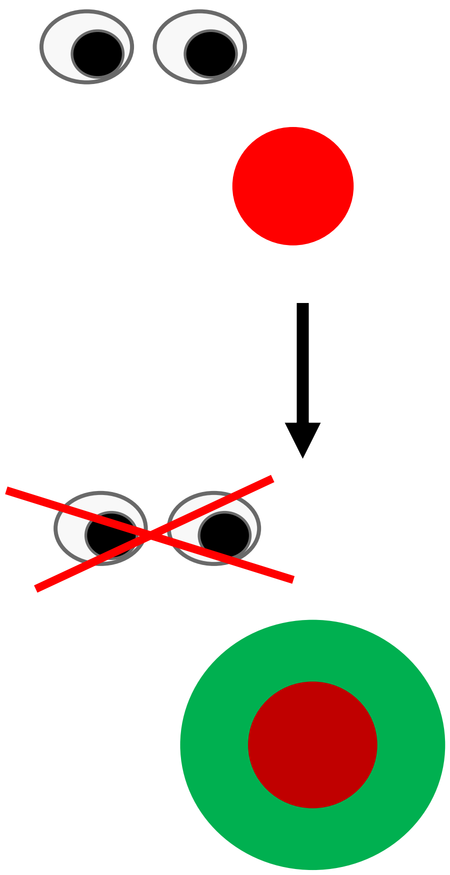


Experimental 2-MT ▪ Experimental 2-MTS ▪ Base Model 2-MT ----- Base Model 2-MTS -----
PS Model 2-MT - - - - - PS Model 2-MTS - - - - -

Conversion of inorganic to organic sulfate reduces predicted acidity when organics are not accounted for in thermodynamic models

ISORROPIA II





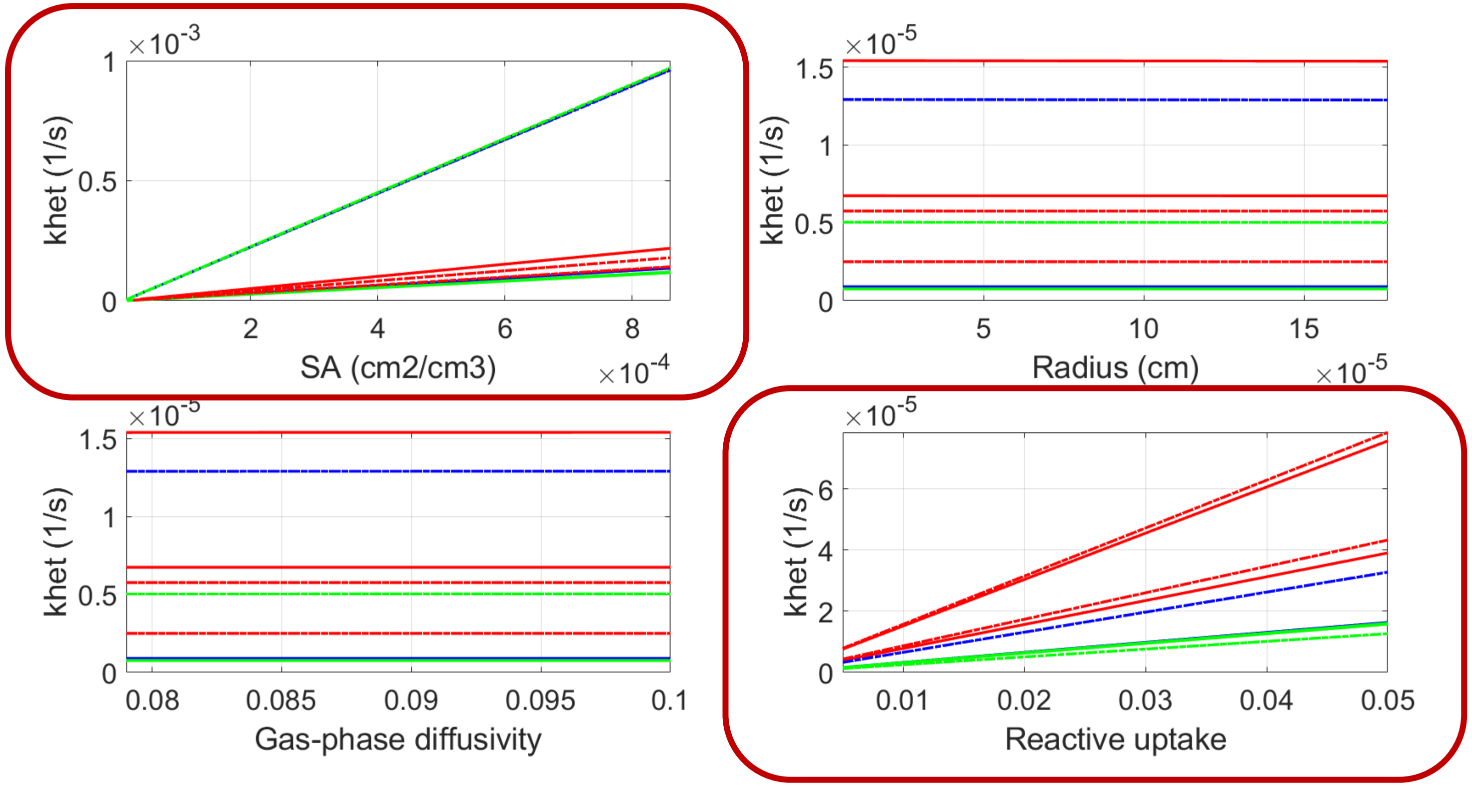
Homogeneous ----- **Phase separated - - - -**

Heterogeneous rate constant sensitivity

- Constant parameters at time = 50 minutes
- Heterogeneous rate constant as a function of high and low literature values
- Flat line = insensitive

$$\mathrm{IEPOX}_{gas} \rightarrow IEPOXSOA_{aero}$$

$$k_{het} = \frac{SA}{\frac{r_p}{D_g} + \frac{4}{\vartheta \gamma}}$$



High IEPOX:Sulfate ----- Mid IEPOX:Sulfate ----

Low IEPOX:Sulfate ------

Parameter	Average Percent Change
Surface area ($cm^2 cm^{-3}$)	**1.00×10^4**
Reactive uptake	**894**
Particle radius (cm)	-0.106
Gas-phase diffusivity ($cm^2 s^{-1}$)	0.023

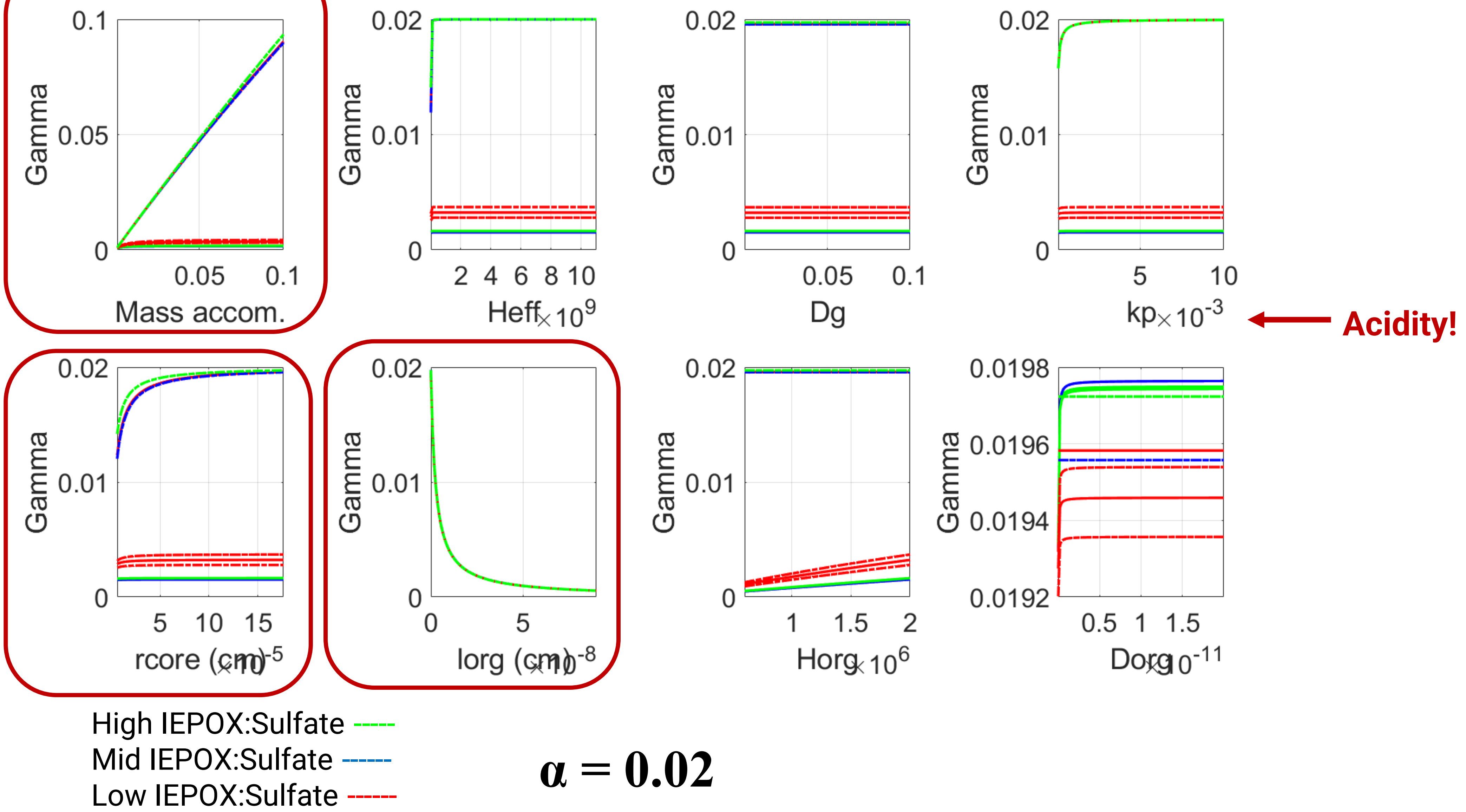
Reactive uptake (χ)

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{v r_p^2}{4 H_{inorg} R T D_a r_{core}} \frac{1}{q \coth(q) - \frac{1}{q}} + \frac{v l_{org} r_p}{4 H_{org} R T D_{org,eff} r_{core}}$$

mass accommodation

gas-phase diffusion

organic coating diffusion limitations



$\alpha = 0.02$

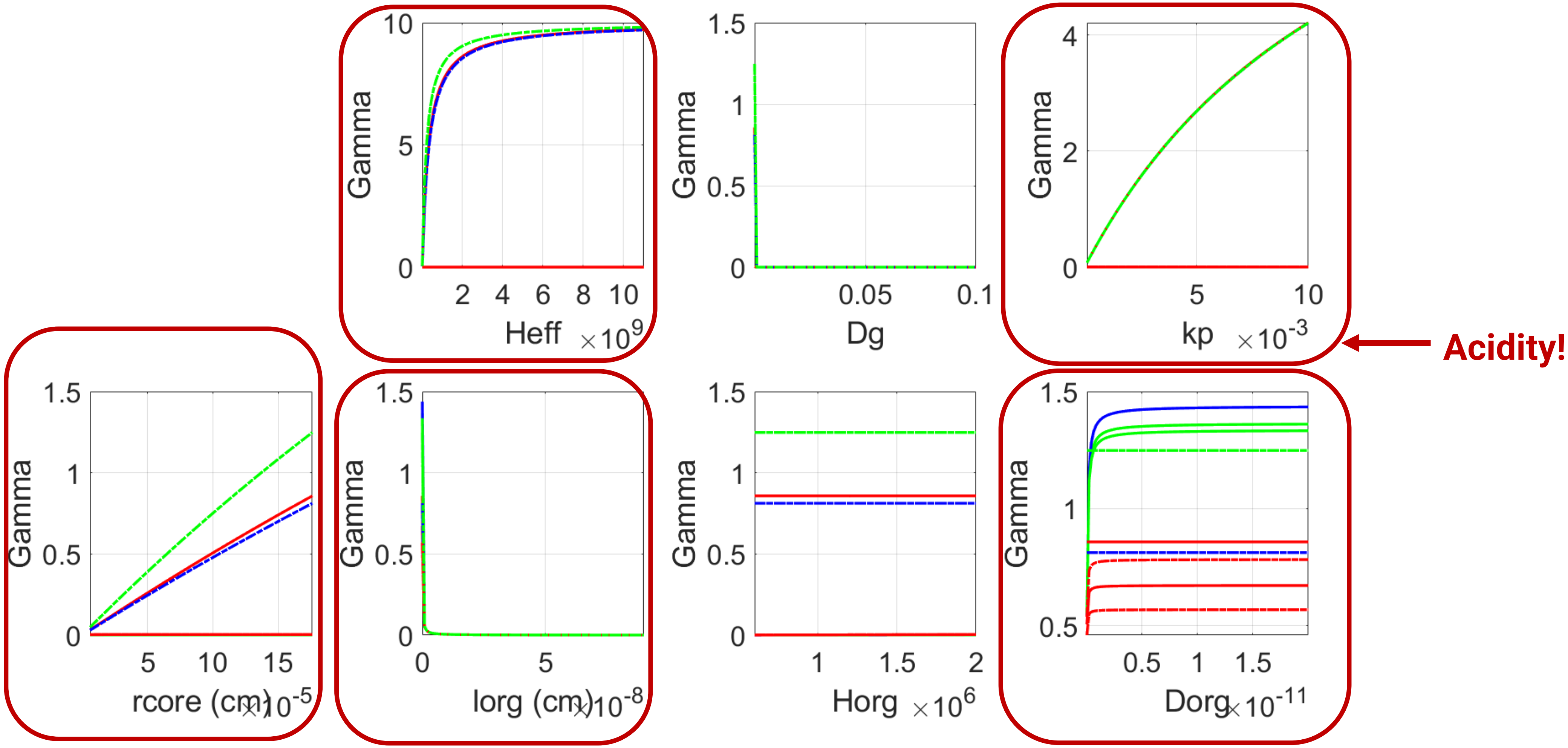
Reactive uptake (γ)

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{v r_p^2}{4 H_{inorg} RT\, D_a r_{core}} \frac{1}{q \coth(q) - \frac{1}{q}} + \frac{v l_{org} r_p}{4 H_{org} RT\, D_{org,eff} r_{core}}$$

mass accommodation

gas-phase diffusion

organic coating diffusion limitations



High IEPOX:Sulfate

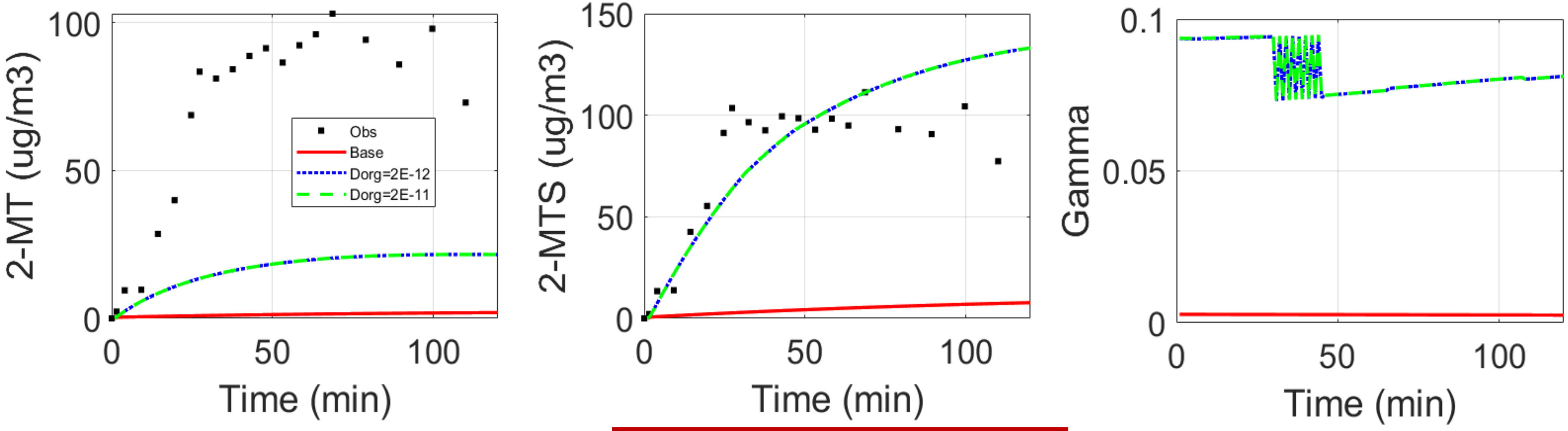
Mid IEPOX:Sulfate

Low IEPOX:Sulfate

$\alpha = 10$

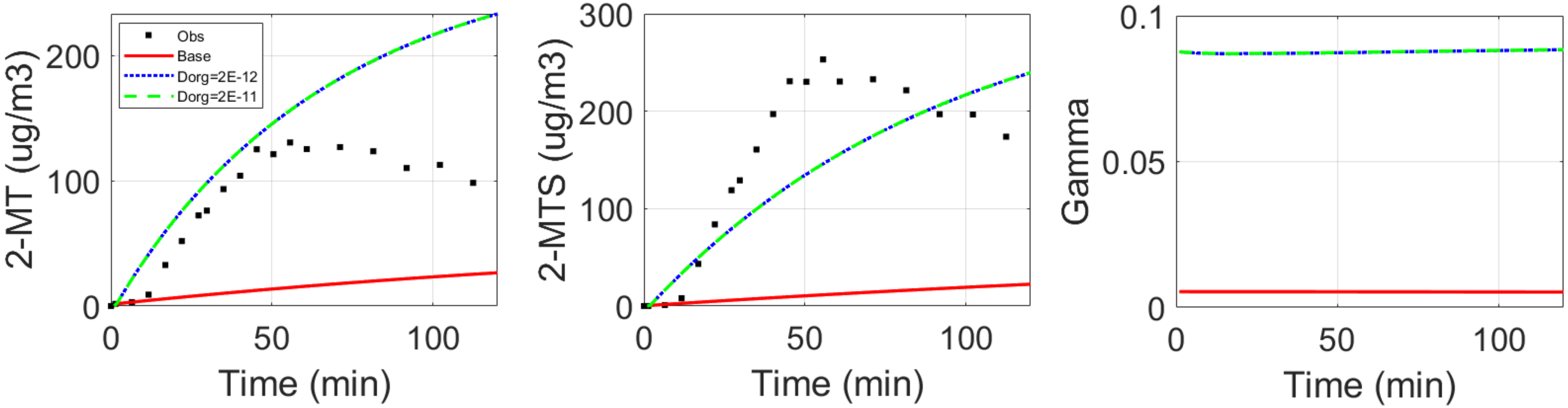
Model prediction improved with increased organic shell diffusivity

IEPOX:Sulf = 10.5



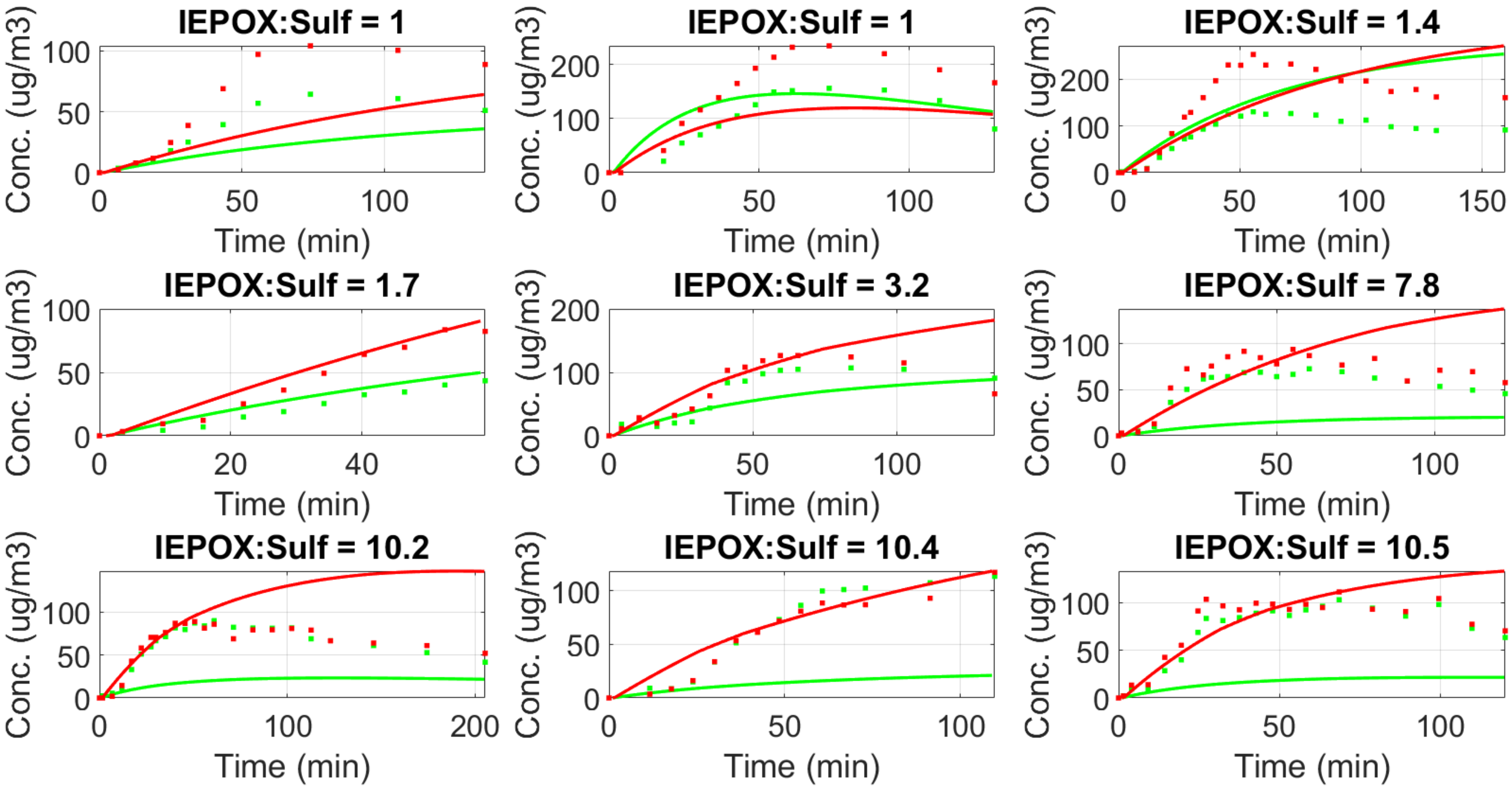
α = 0.1

IEPOX:Sulf = 1.4



α = 0.1

Utilizing homogeneous and phase state/separation reactive uptake for different reactions improved model performance



Homogeneous

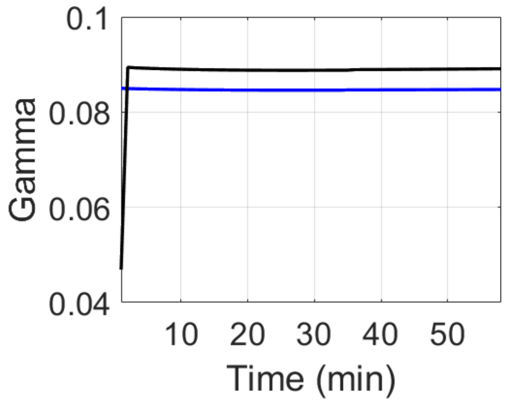
$IEPOX + H_2O + H^+ \rightarrow 2MT$

$IEPOX + SO_4^{2-} + H^+ \rightarrow 2MTS$

Phase separated

$IEPOX + 2MT + H^+ \rightarrow Dimer$

$IEPOX + 2MTS + H^+ \rightarrow Dimer$



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Base Model 2-MT
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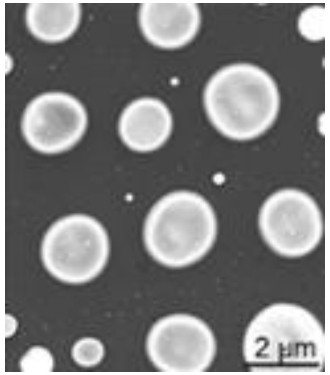
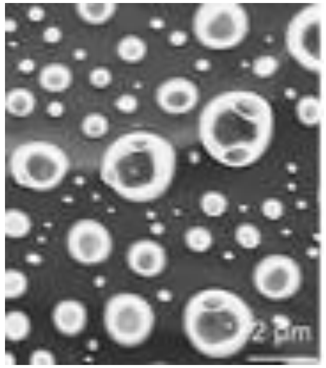
Connecting experimental findings with regional-scale modeling and application





The most sensitive model parameters were:

- Mass accommodation
- Particle size (surface area, radius, shell thickness)
- Diffusivity through the organic shell

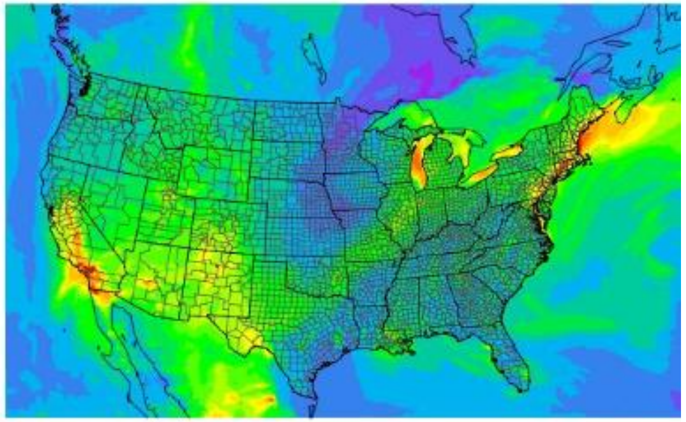
Phase state/separation reactive uptake model has **little sensitivity to acidity changes**

Increasing organic shell diffusivity resulted in improved model performance

Utilizing **two separate coefficients for reactive uptake of IEPOX to acidified sulfate and pre-existing IEPOX SOA** improved model performance

Modeling performance differed for **high and low IEPOX:Sulfate ratios.** As natural and anthropogenic emissions change, IEPOX:Sulfate is expected to increase.

Future work: *Implement improved model in regional-scale*



Thank You!

Collaborators: Yuzhi Chen, Jaime Green, Jason D. Surratt, Haofei Zhang, Will Vizuete

Contact: **Alexandra.Ng@unc.edu**