AQRP WORKSHOP

Update and evaluation of model algorithms needed to predict Particulate Matter from Isoprene

William Vizuete
Jason Surratt

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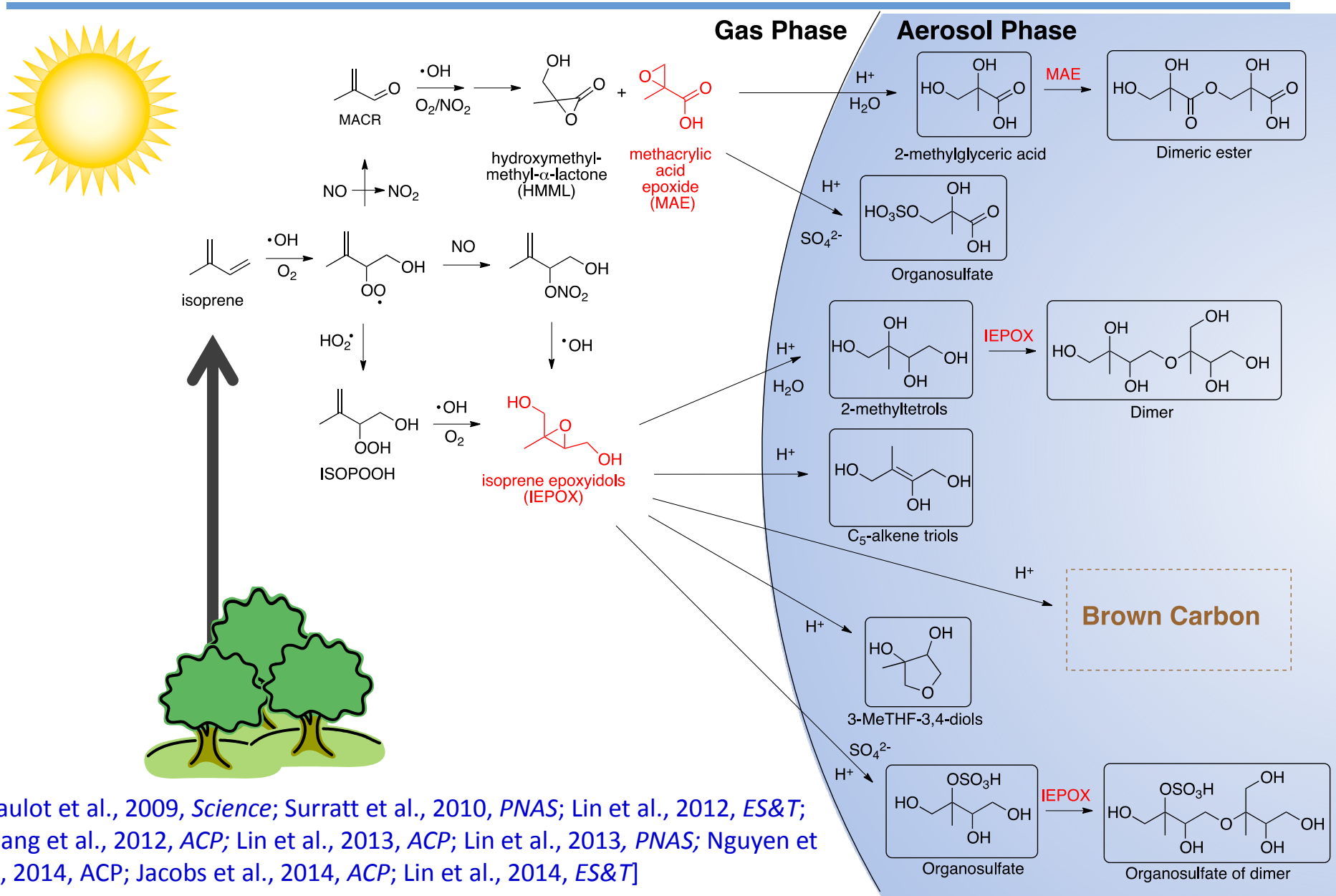
Isoprene-Derived Epoxides Promote SOA Formation



[Paulot et al., 2009, *Science*; Surratt et al., 2010, *PNAS*; Lin et al., 2012, *ES&T*; Zhang et al., 2012, *ACP;* Lin et al., 2013, *ACP*; Lin et al., 2013, *PNAS;* Nguyen et al., 2014, ACP; Jacobs et al., 2014, *ACP*; Lin et al., 2014, *ES&T*]

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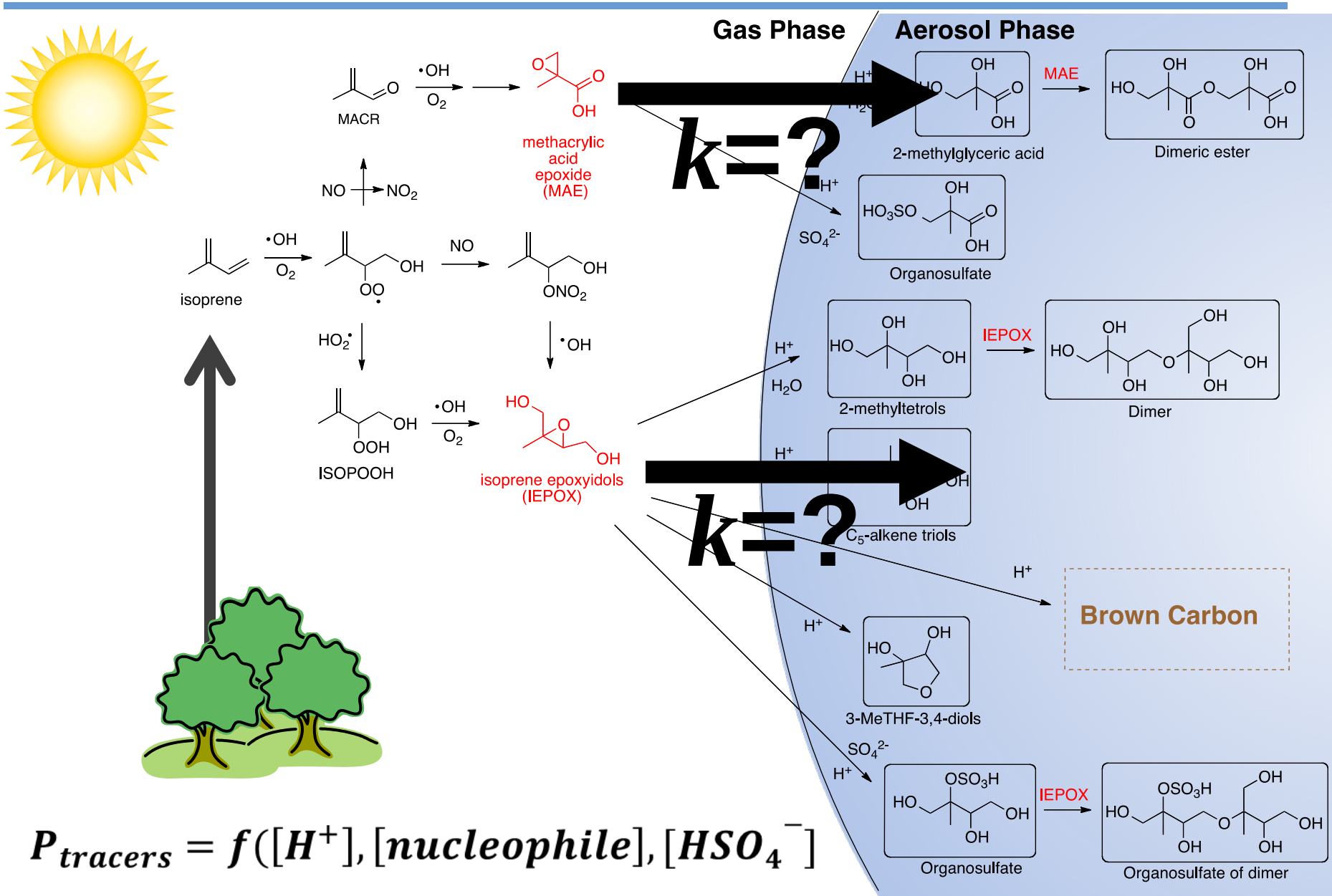
Isoprene-Derived Epoxides Are Critical in SOA Formation from Isoprene Oxidation



$$P_{tracers} = f([H^+], [nucleophile], [HSO_4^-])$$

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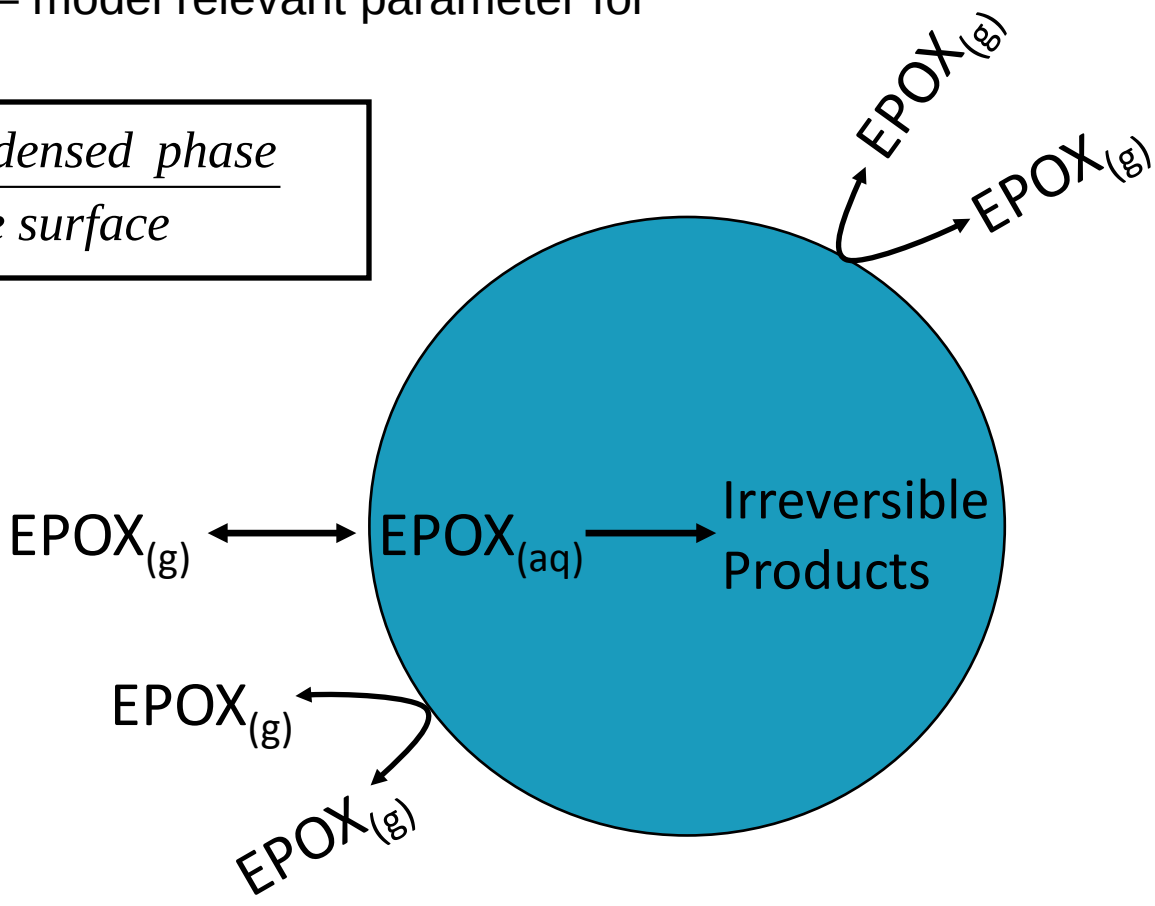
What is the Reactive Flux to Particles?

Gas-Aerosol Reaction Probability – model relevant parameter for heterogeneous chemistry

$$\gamma = \frac{\#\ molecules\ removed\ by\ condensed\ \ phase}{\#\ molecules\ striking\ the\ surface}$$

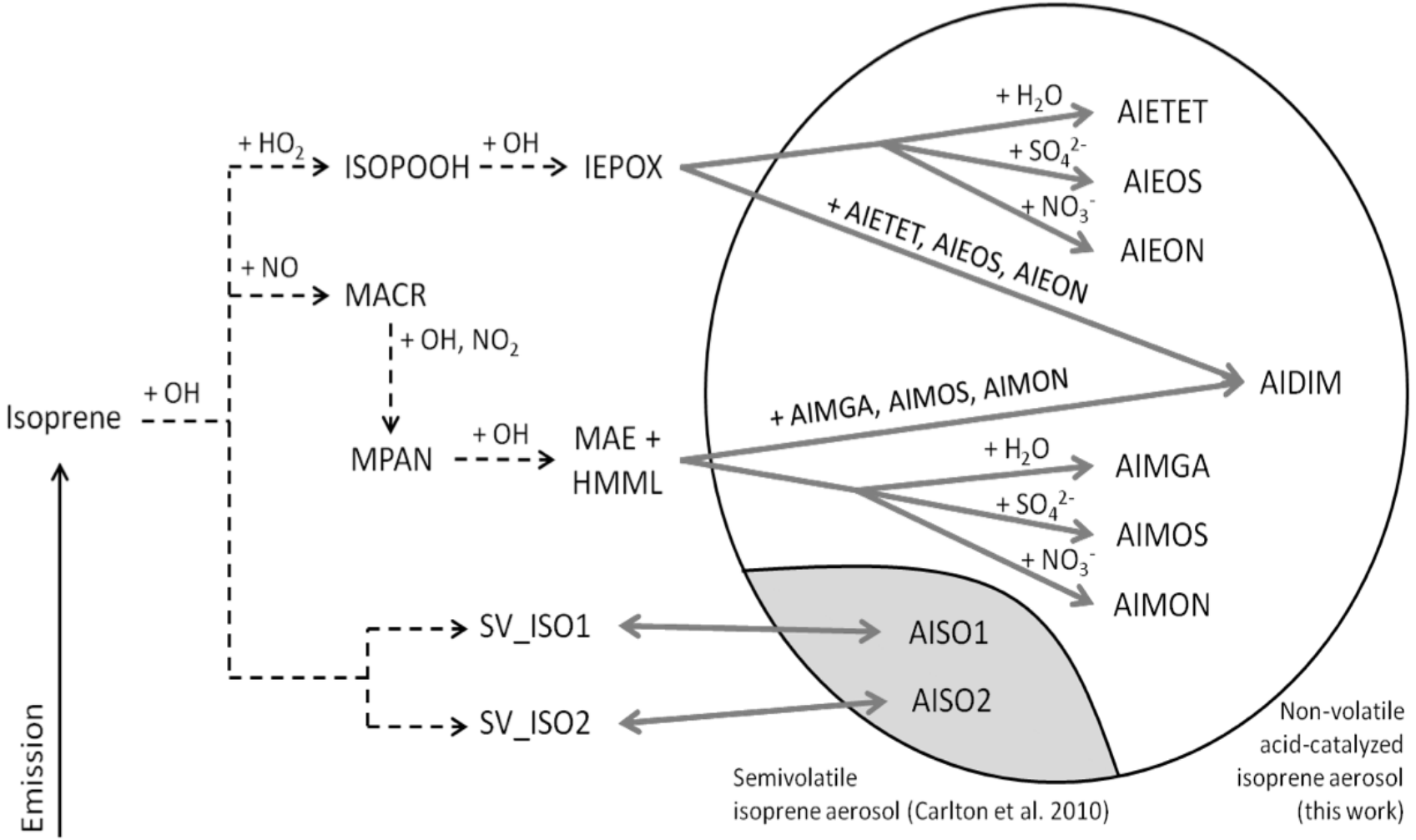


$$\frac{d[EPOX]}{dt} = k_{het}[EPOX]$$

$$= \gamma \frac{S_a \omega}{4} [EPOX]$$

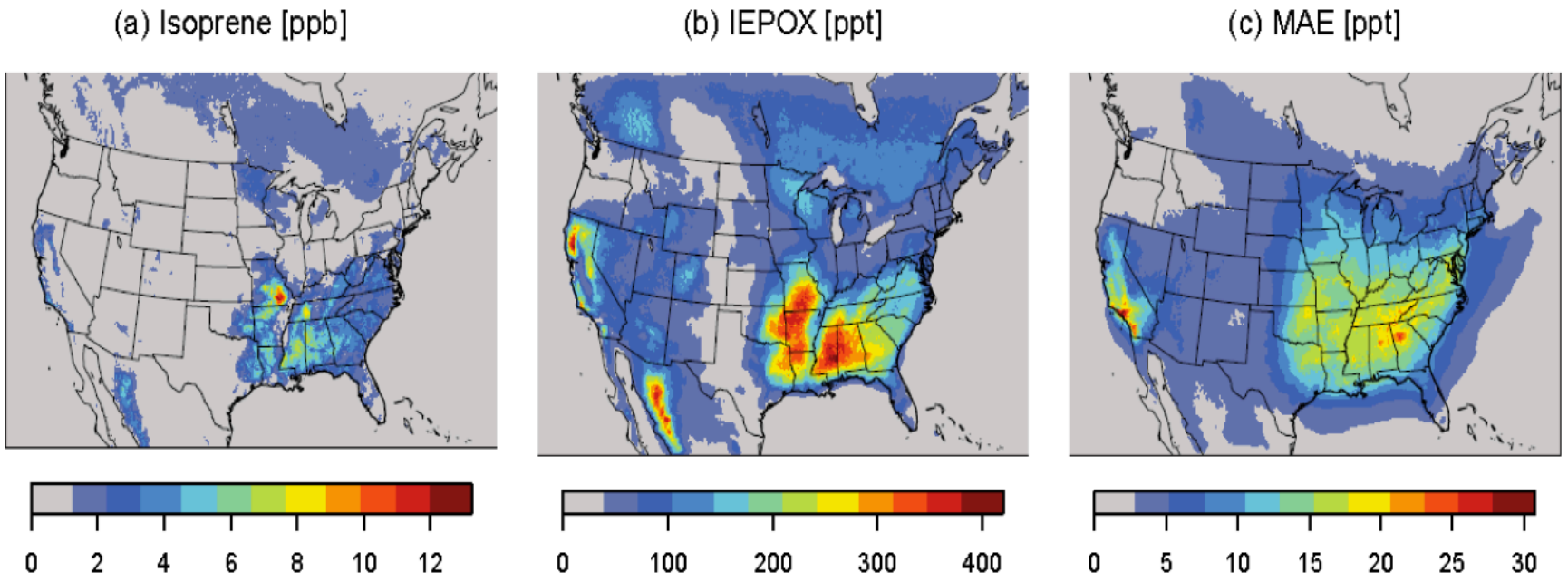
collision frequency

Model Implementation



dx.doi.org/10.1021/es402106h | *Environ. Sci. Technol.* 2013, 47, 11056−11064

Model Implementation



ENVIRONMENTAL Science & Technology

Article

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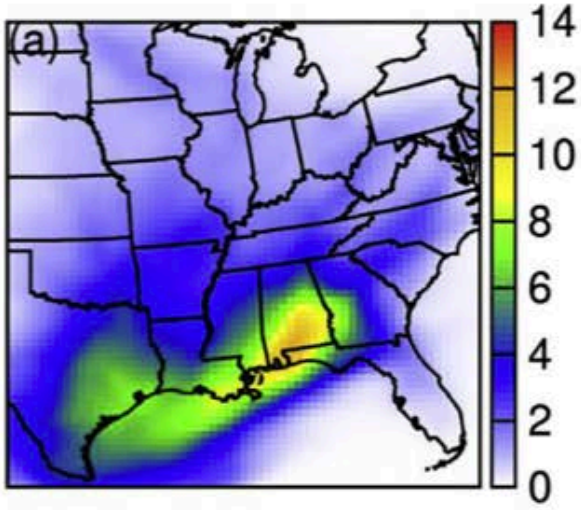
dx.doi.org/10.1021/es402106h | *Environ. Sci. Technol.* 2013, 47, 11056−11064

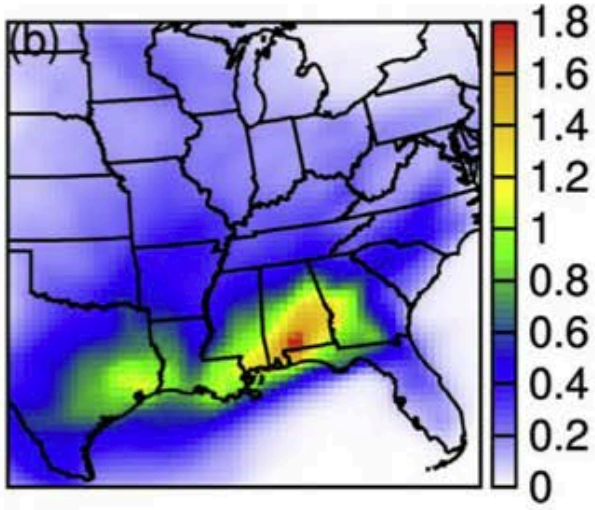
Epoxide Pathways Improve Model Predictions of Isoprene Markers and Reveal Key Role of Acidity in Aerosol Formation

Havala O. T. Pye,*[,†] Robert W. Pinder,[†] Ivan R. Piletic,[†] Ying Xie,[†,‡] Shannon L. Capps,[†] Ying-Hsuan Lin,[¶] Jason D. Surratt,[¶] Zhenfa Zhang,[¶] Avram Gold,[¶] Deborah J. Luecken,[†] William T. Hutzell,[†] Mohammed Jaoui,[§] John H. Offenberg,[†] Tadeusz E. Kleindienst,[†] Michael Lewandowski,[†] and Edward O. Edney[†]

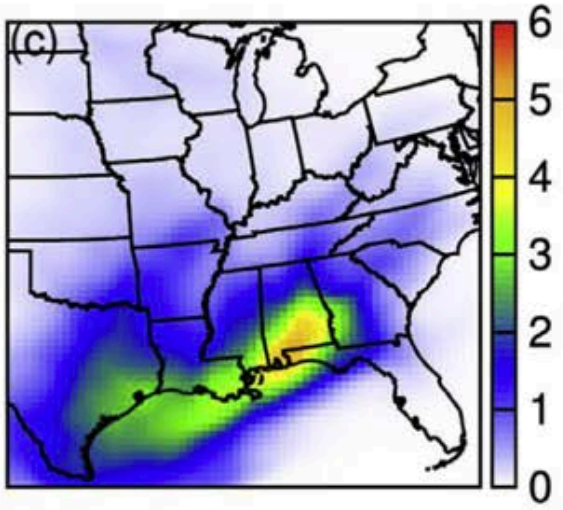
Model Implementation



Total SOA



SV-SOA



EPOX-SOA

Atmospheric Environment 102 (2015) 52–61

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Modeling regional secondary organic aerosol using the Master Chemical Mechanism

Jingyi Li [a], Meredith Cleveland [b], Luke D. Ziemba [c], Robert J. Griffin [d], Kelley C. Barsanti [e], James F. Pankow [e], Qi Ying [a, *]

Proposal Objectives

Task 1. Integration of Gas-Phase Epoxide Formation and Subsequent SOA Formation into UNC MORPHO Box Model

Task 2. Synthesis of Isoprene-derived Epoxides and Known SOA Tracers

Task 3. Indoor Chamber Experiments Generating SOA Formation Directly from Isoprene-Derived Epoxides

Task 4. Modeling of Isoprene-derived SOA Formation From Environmental Simulation Chambers

Task 1 – Gas Phase Evaluation

Atmospheric Environment 105 (2015) 109–120

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Assessment of SAPRC07 with updated isoprene chemistry against outdoor chamber experiments

Yuzhi Chen, Kenneth G. Sexton, Roger E. Jerry, Jason D. Surratt, William Vizuete*

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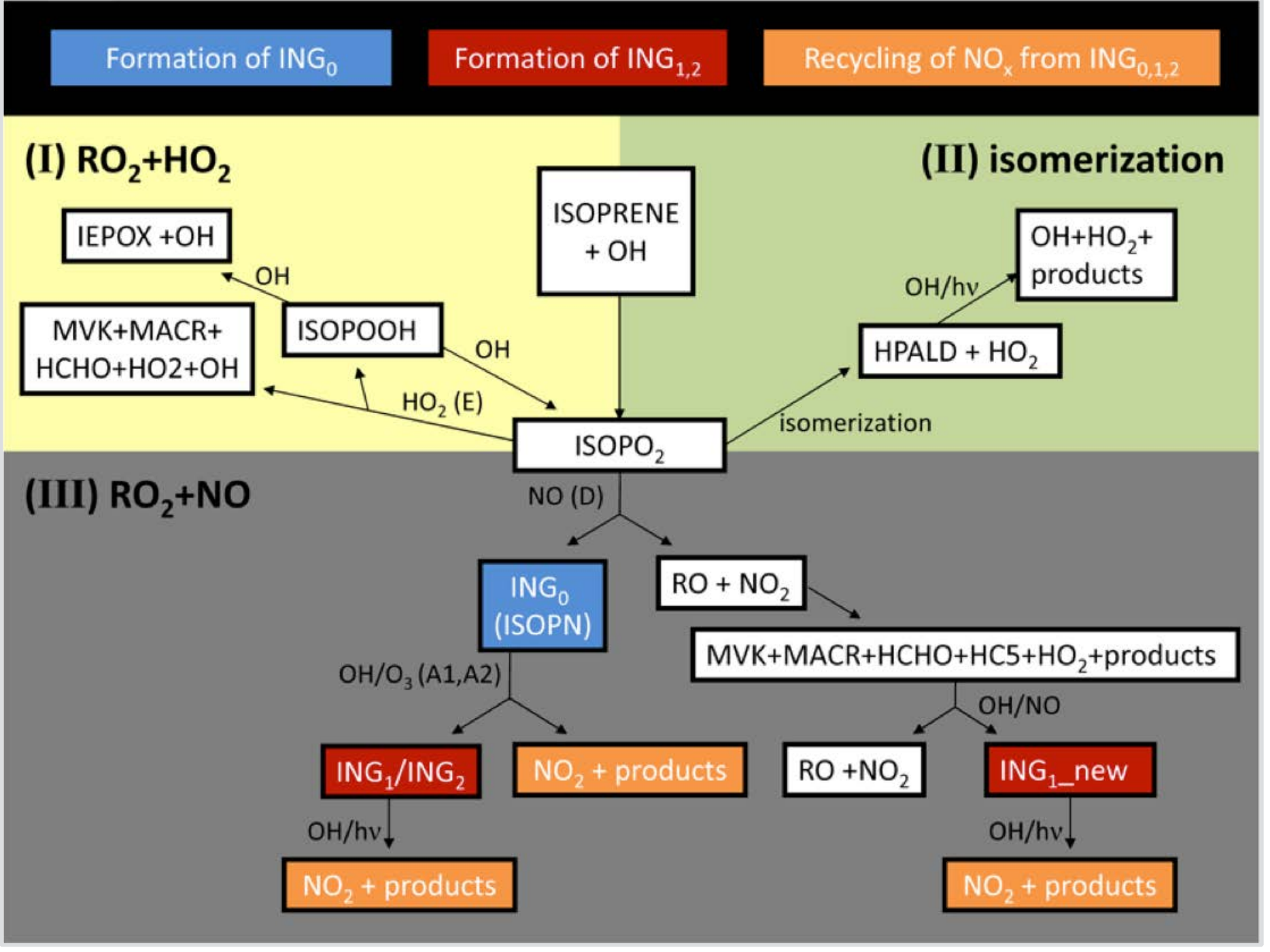


[Xie et al., 2013, ACP]

Task 1 – Gas Phase Evaluation

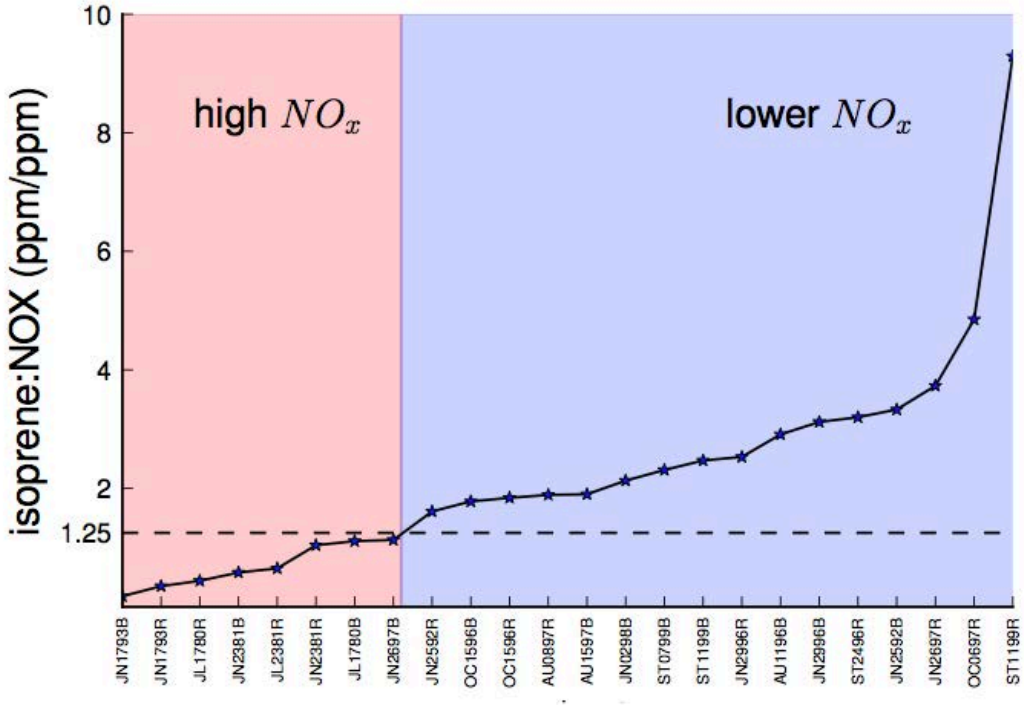
UNC dual gas-phase chamber, Pittsboro, NC, 1994

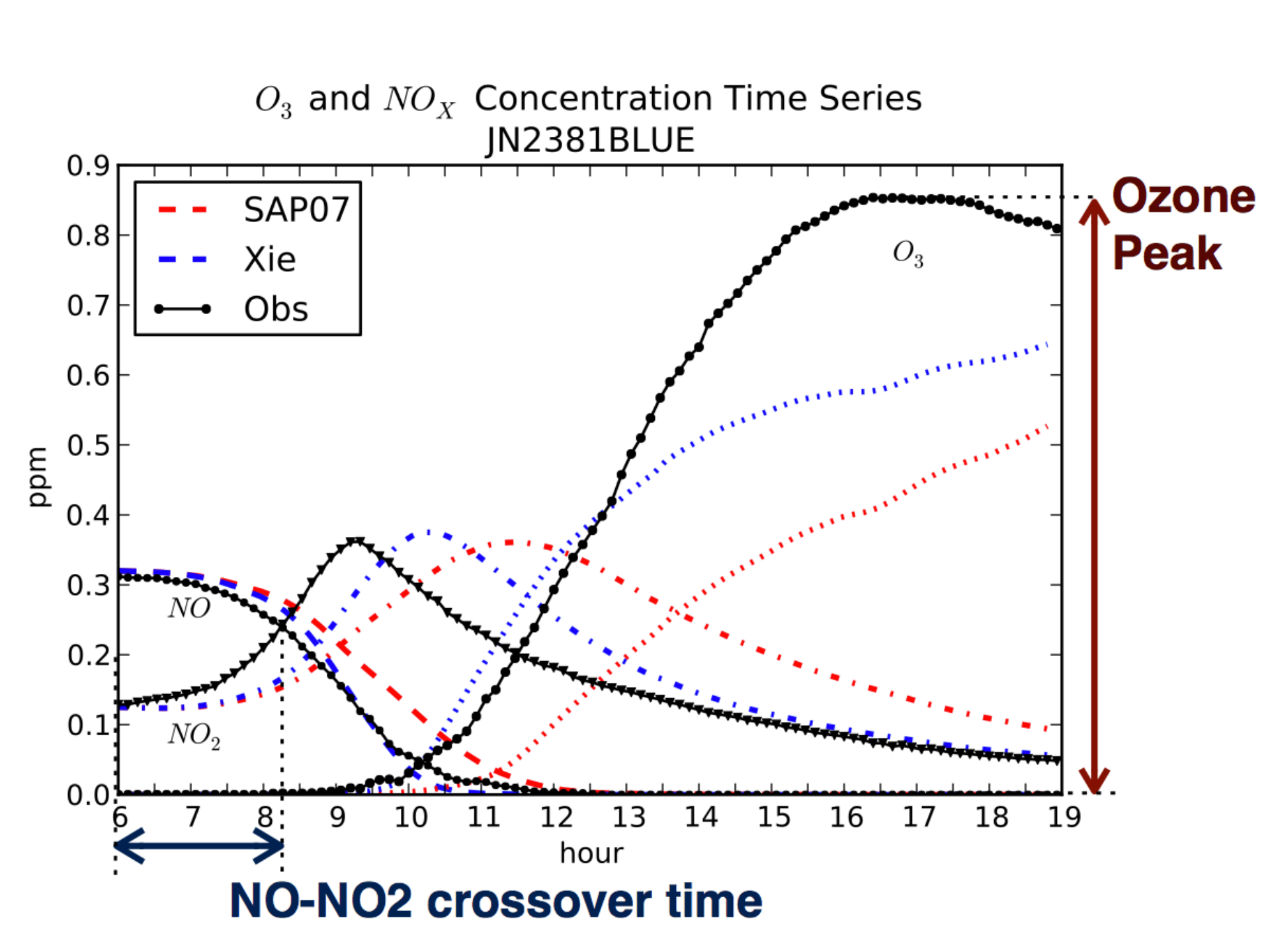
Experimental:

- 16 characterization runs
- 24 isoprene runs
- Compounds measured: O_3, NO, NO_2, Isoprene,CO, HCHO, PAN…

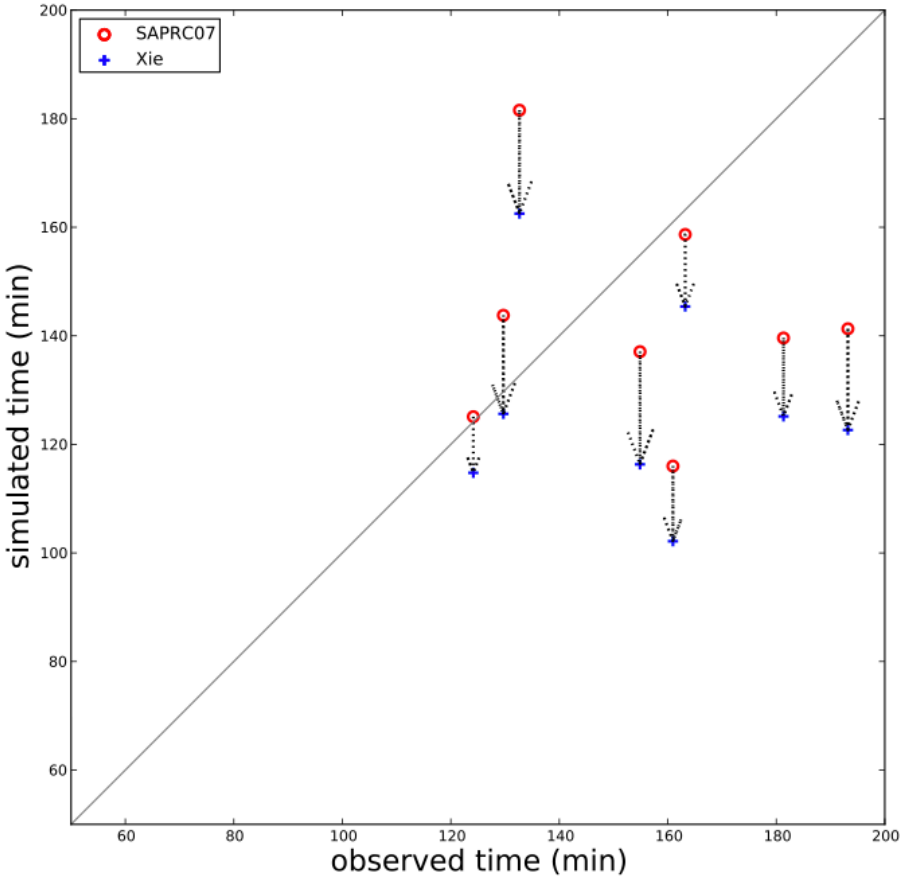
Modeling:

- MORPHO (UNC)



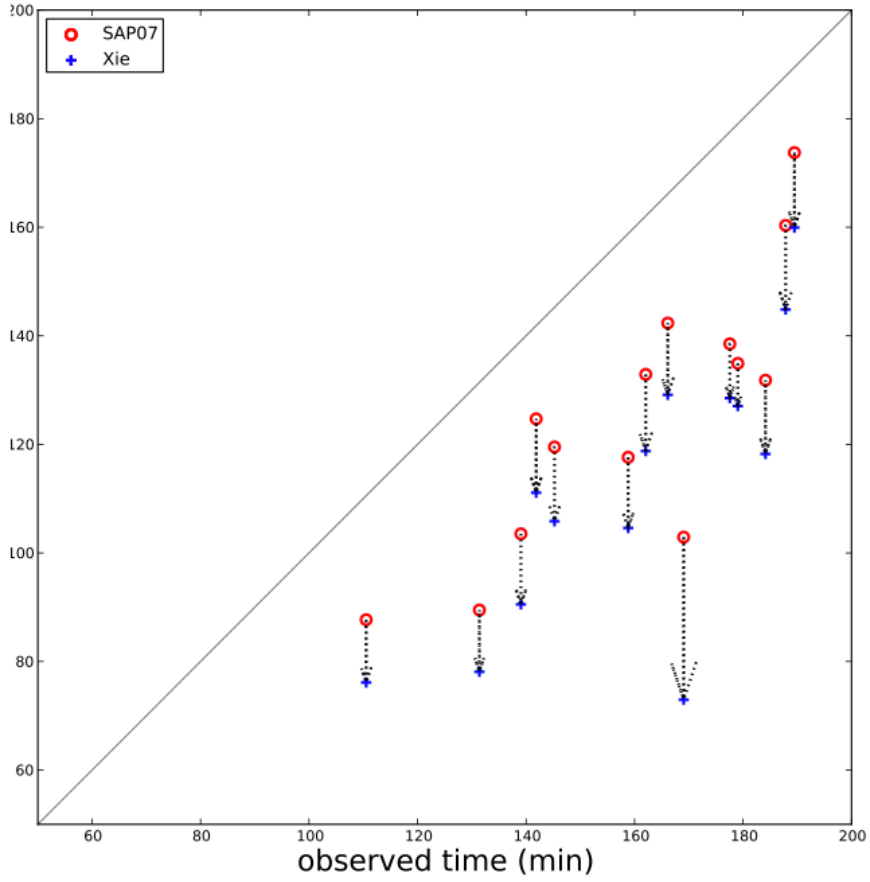

O_3 and NO_X Concentration Time Series
JN2381BLUE
SAP07
Xie
Obs
O_3
NO
NO_2
ppm
hour
Ozone Peak
NO-NO2 crossover time

High NO_X



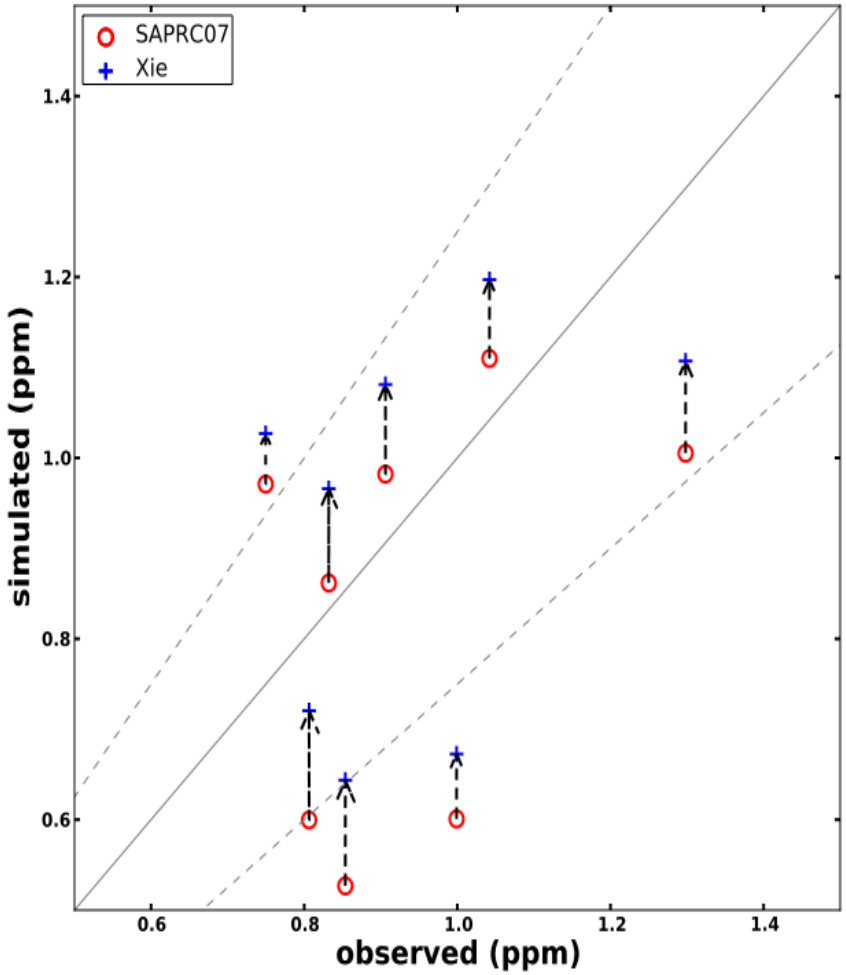
Mech	NMB(%)	R^2
SAPRC07	-5.4	0.022
Xie	**-16.0**	0.032

Lower NO_X

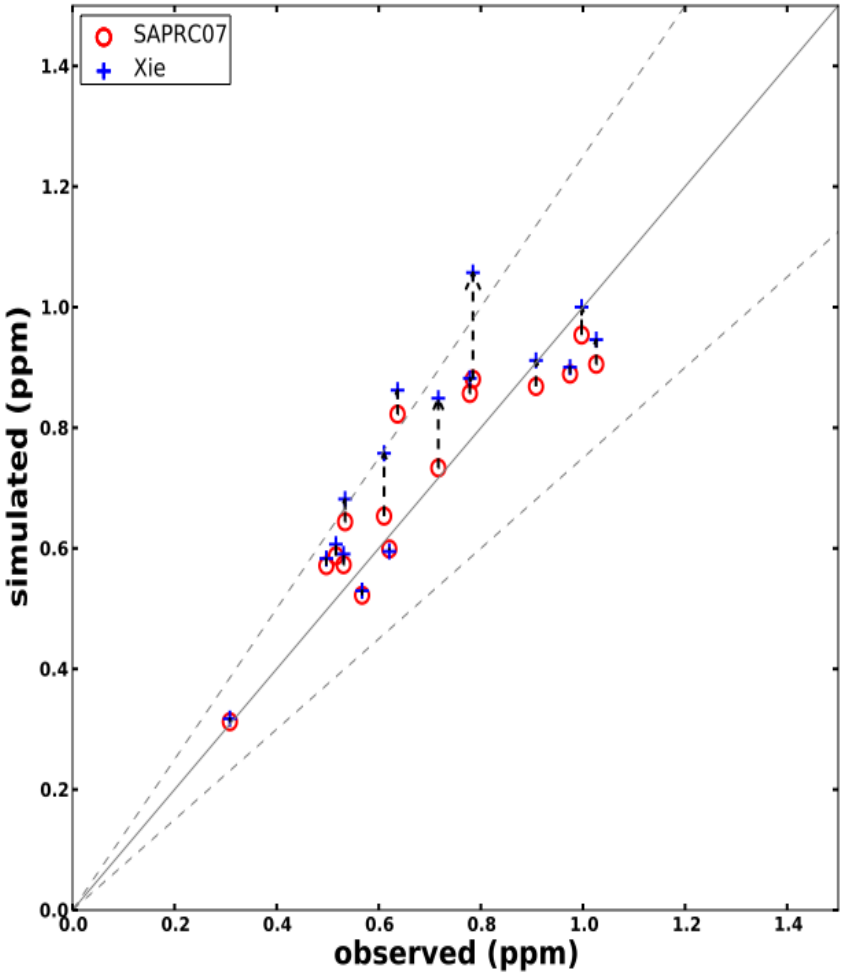


Mech	NMB(%)	R^2
SAPRC07	-24.1	0.77
Xie	**-32.3**	0.68

High NO_X



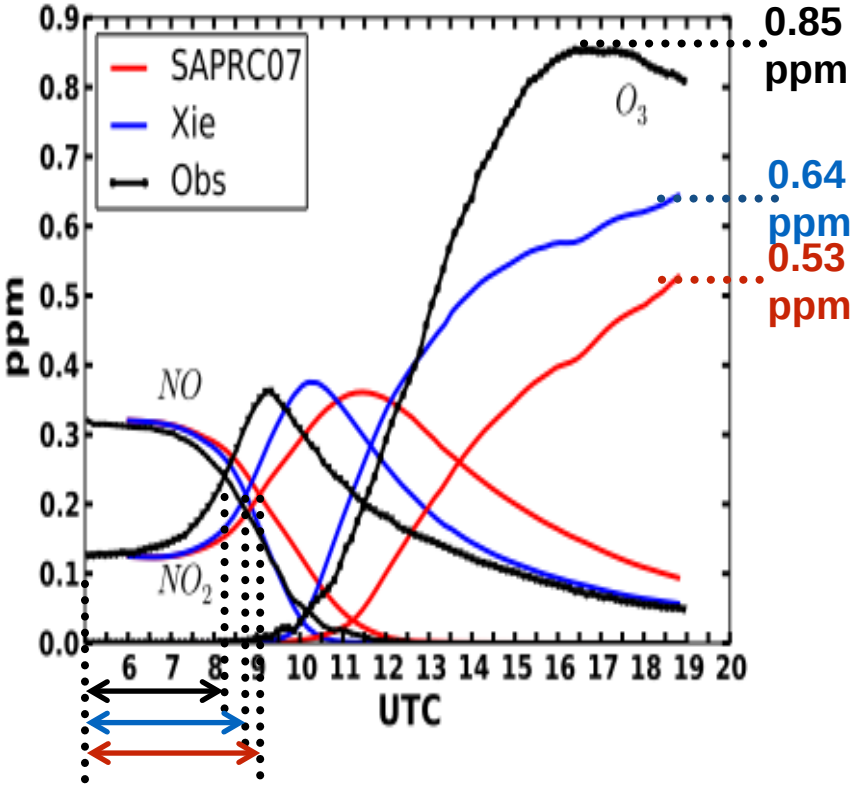
Lower NO_X

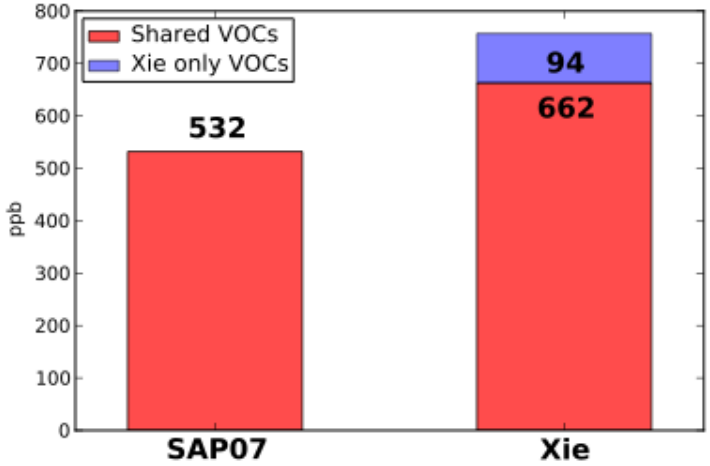


Mech	NMB(%)	R^2	P value
SAPRC07	-9.79	0.13	0.38
Xie	0.58	0.14	0.36

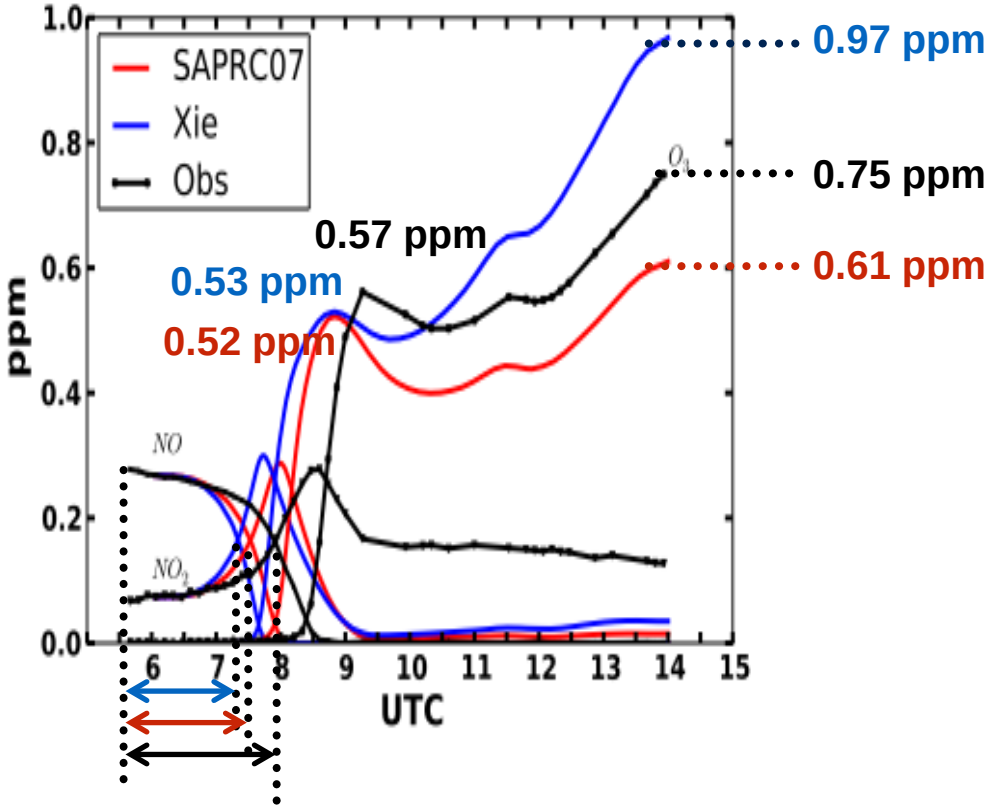
Mech	NMB (%)	R^2	P value
SAPRC07	4.92	0.85	9.51E-06
Xie	11.08	0.76	1.42E-16

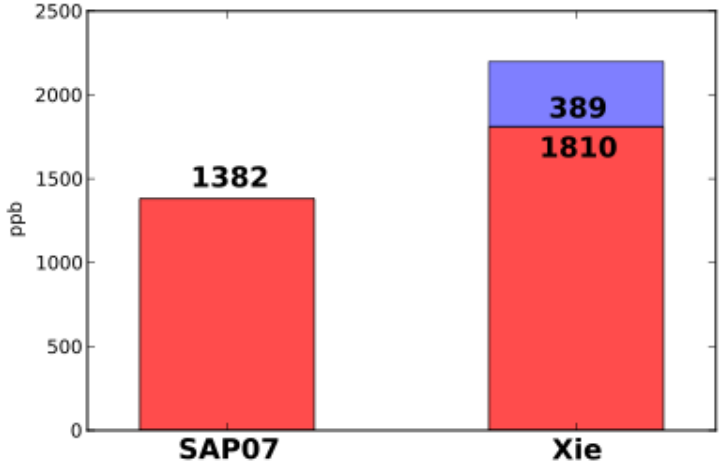
High NO_X





Lower NO_X

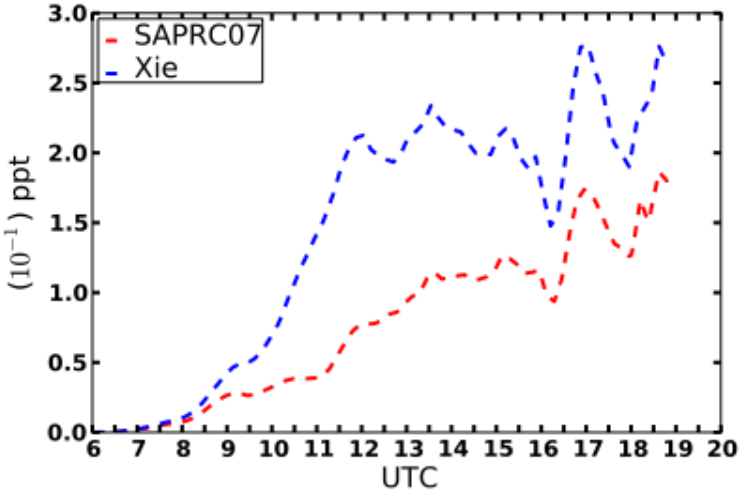


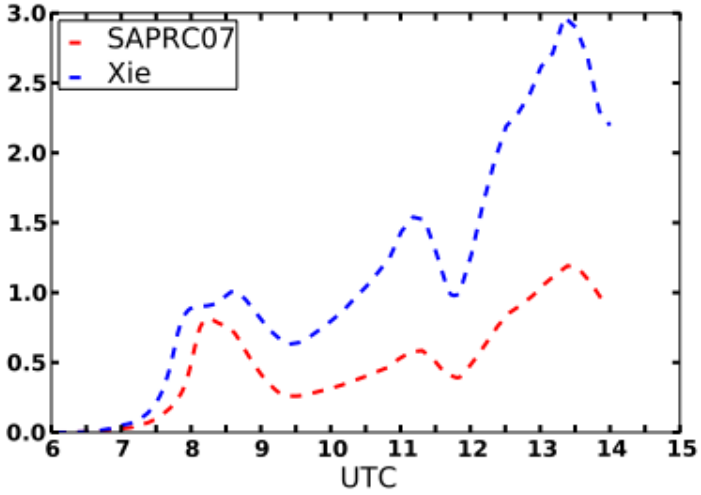


High NO_X

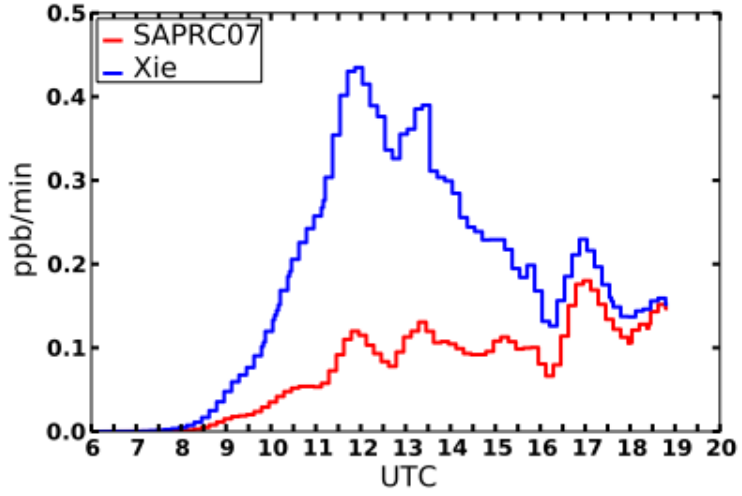
Lower NO_X

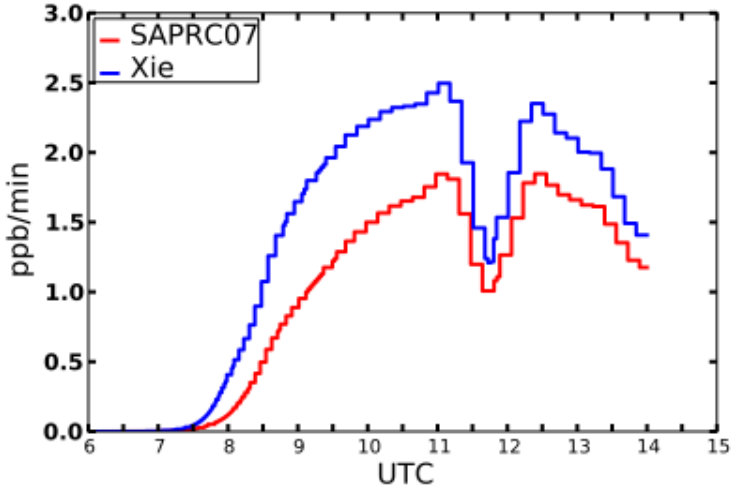
OH conc.





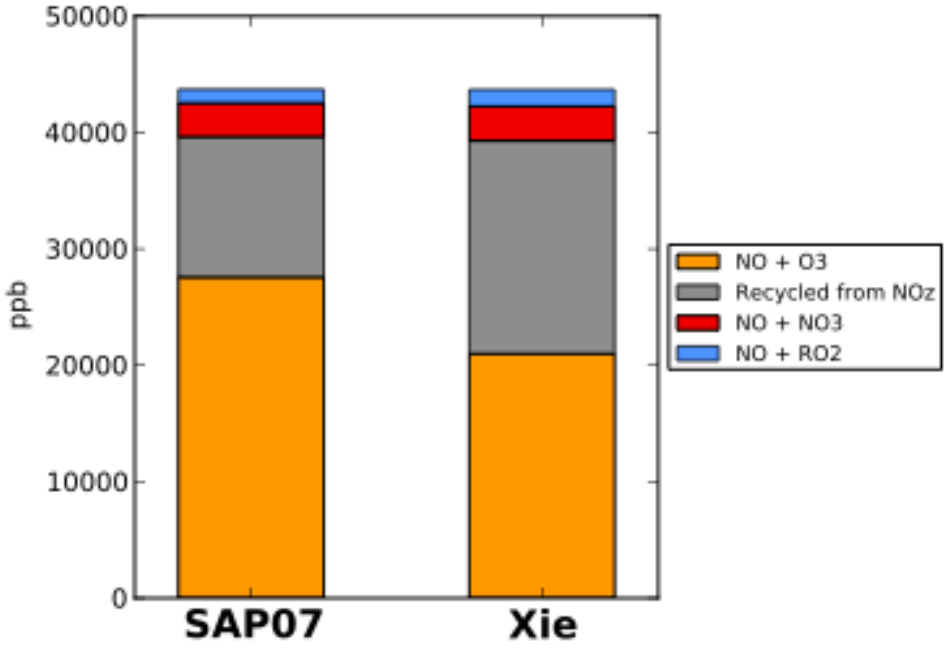
HO_2 from Aldehydes



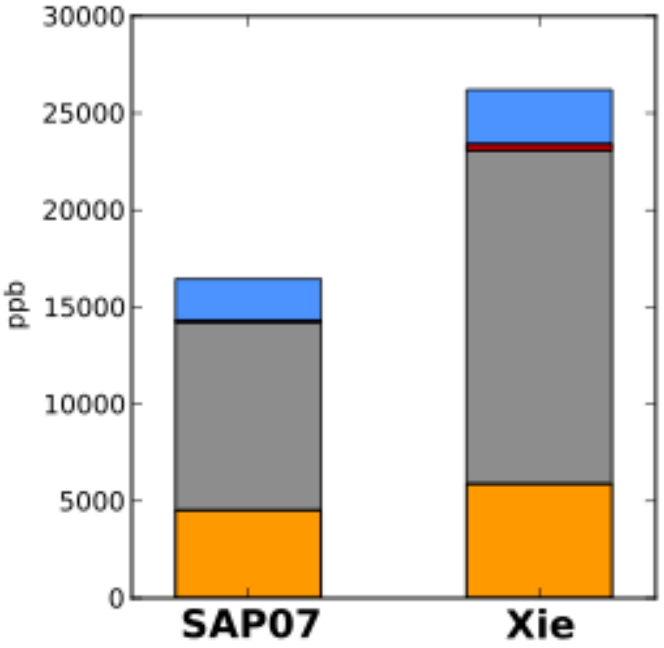


Sources of NO_2

High NOx



Lower NOx

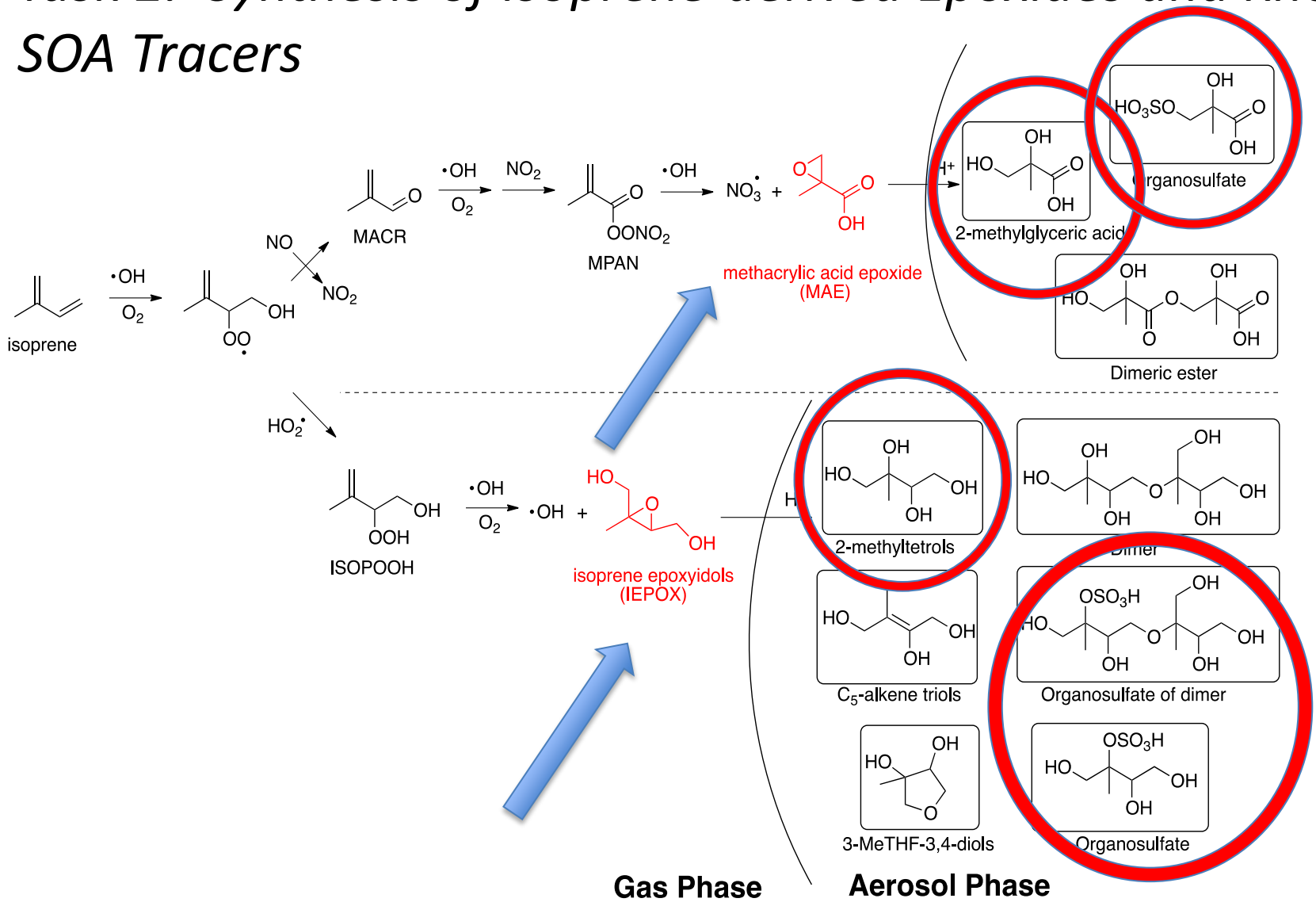


- *High NO_X* — 65% NO_2 made through NO + O3 for SAPRC07; 47% made through recycling from NO_Z for Xie

- *Lower NO_X* — 77% more NO2 recycled from NO_Z for Xie

Proposal Objectives

Task 2. Synthesis of Isoprene-derived Epoxides and Known SOA Tracers



Proposal Objectives

Task 3. Indoor Chamber Experiments Generating SOA Formation Directly from Isoprene-Derived Epoxides

Expt. #	Epoxide	[Epoxide] (ppb)	Seed Aerosol Type	Initial Seed Aerosol ($\mu g/m^3$)	RH (%)	T (°C)
1	IEPOX	300	$(NH_4)_2SO_4$	~20-30	~50-60	~20-25
2		300	$(NH_4)_2SO_4 + H_2SO_4$	~20-30	~50-60	~20-25
3	MAE	300	$(NH_4)_2SO_4$	~20-30	~50-60	~20-25
4		300	$(NH_4)_2SO_4 + H_2SO_4$	~20-30	~50-60	~20-25
5	none		$(NH_4)_2SO_4$	~20-30	~50-60	~20-25
6	none		$(NH_4)_2SO_4 + H_2SO_4$	~20-30	~50-60	~20-25
7	IEPOX	300	none	none	~50-60	~20-25
8	MAE	300	none	none	~50-60	~20-25

0.6 M (NH4)2SO4 + 0.6 M H2SO4

Proposal Objectives

Task 4. Modeling of Isoprene-derived SOA Formation From Environmental Simulation Chambers

ENVIRONMENTAL Science & Technology LETTERS

DOI: 10.1021/ez500406f
Environ. Sci. Technol. Lett. 2015, 2, 38–42

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Letter

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Heterogeneous Reactions of Isoprene-Derived Epoxides: Reaction Probabilities and Molar Secondary Organic Aerosol Yield Estimates

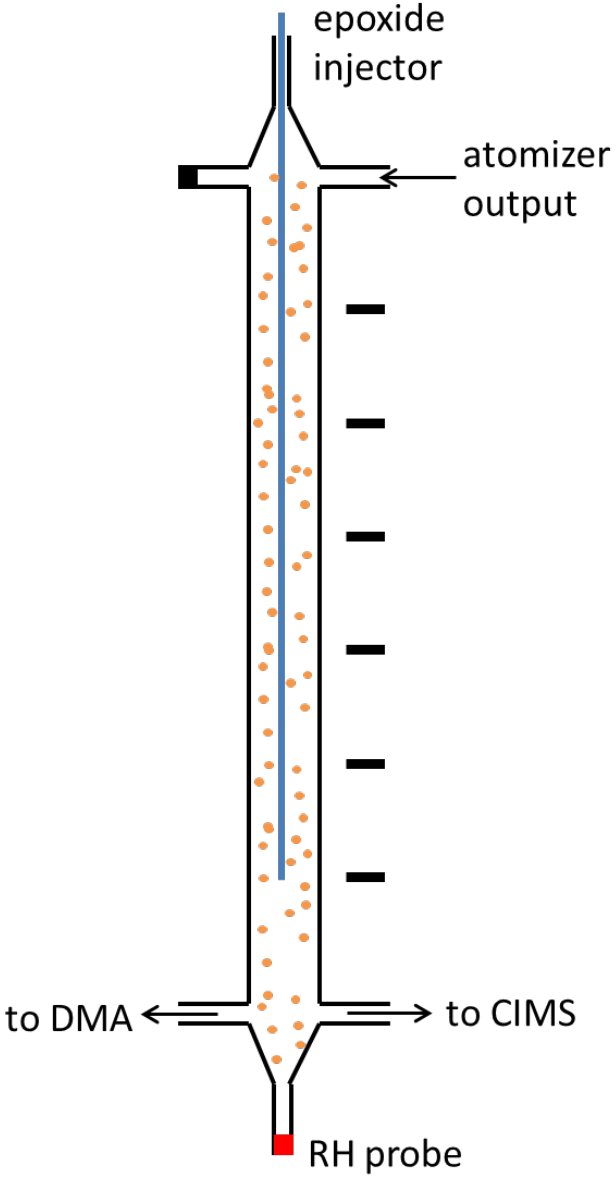
Theran P. Riedel,[†] Ying-Hsuan Lin,[†] Sri Hapsari Budisulistiorini,[†] Cassandra J. Gaston,[‡] Joel A. Thornton,[‡] Zhenfa Zhang,[†] William Vizuete,[†] Avram Gold,[†] and Jason D. Surratt*[,†]

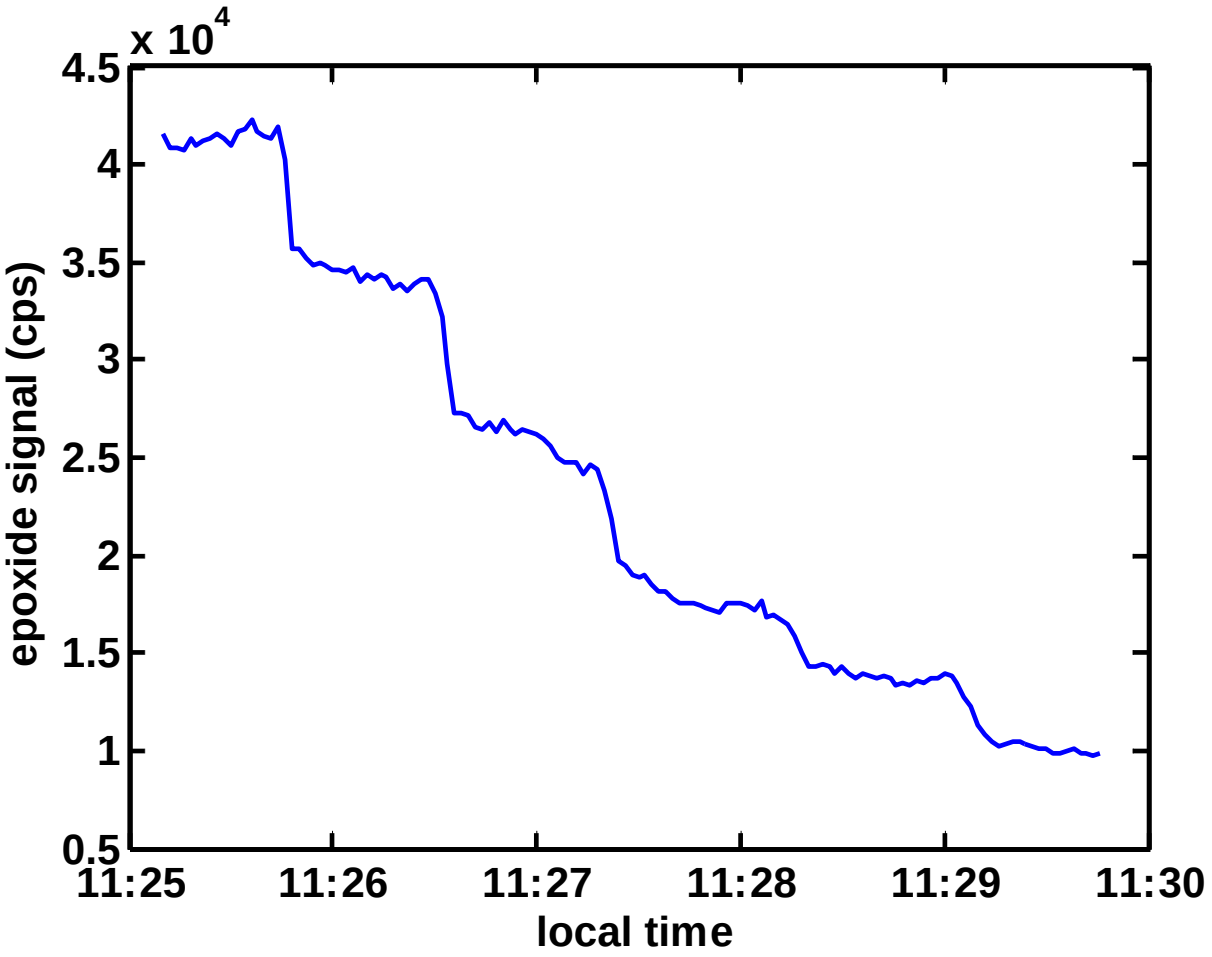
Constraining Condensed-Phase Formation Kinetics of Secondary Organic Aerosol Components from Isoprene Epoxydiols

Theran P. Riedel, Zhenfa Zhang, Kevin Chu, Joel A. Thornton, William Vizuete, Avram Gold, and Jason D. Surratt

Manuscript in preparation

Measuring Reactive Uptake





[Riedel et al., 2015, *ES&T Letters*; Gaston et al., 2014, *ES&T*]

Measuring Reactive Uptake

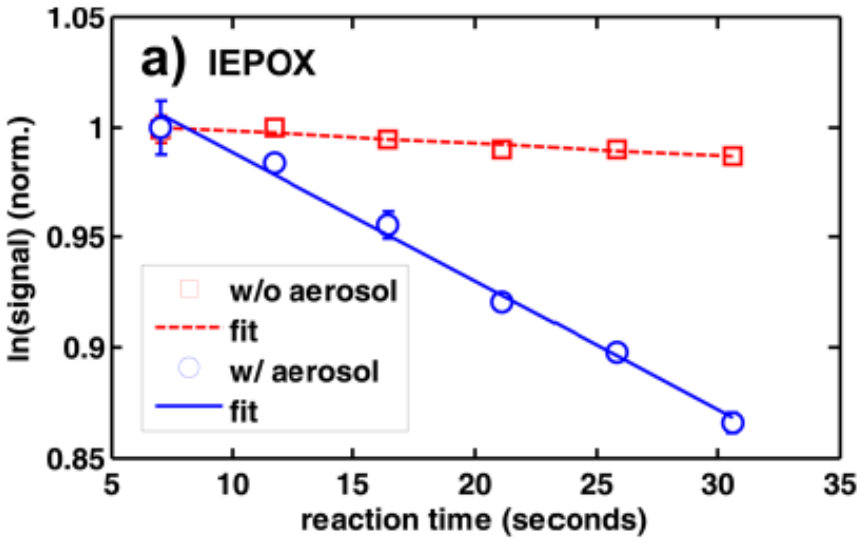
From linear fit:

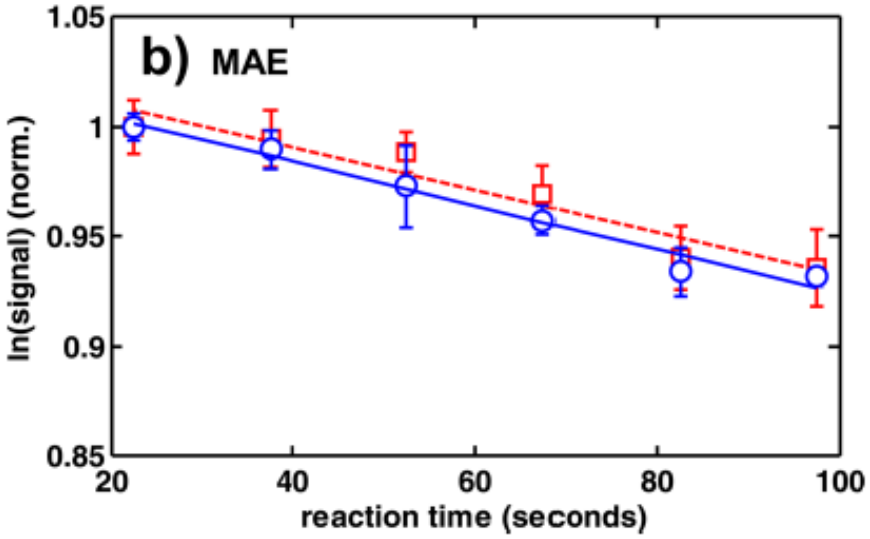
$$k_{total} = -m$$

$$k_{wall} = -m$$

$$k_{total} \approx k_{het} + k_{wall}$$

$$\gamma \approx \frac{4k_{het}}{S_a \omega}$$





[Riedel et al., 2015, *ES&T Letters*]

γ Results

epoxide	aerosol	RH	aerosol $[H^+]$ (M)[a]	$\gamma \pm 1\sigma$
IEPOX	$(NH_4)_2SO_4$	0.50	7.74×10^{-5}	$6.5\times10^{-4} \pm 6.4\times10^{-4}$
IEPOX	$MgSO_4 + H_2SO_4$	0.08	0.04	$1.1\times10^{-2} \pm 3\times10^{-3}$
IEPOX	$MgSO_4 + H_2SO_4$	0.53	0.73	$9.4\times10^{-3} \pm 3\times10^{-3}$
IEPOX	$(NH_4)_2SO_4 + H_2SO_4$	0.05	2.78	$2.1\times10^{-2} \pm 1\times10^{-3}$
IEPOX	$(NH_4)_2SO_4 + H_2SO_4$	0.59	2.01	$1.9\times10^{-2} \pm 2\times10^{-3}$
MAE	$MgSO_4 + H_2SO_4$	0.03	0.73	$4.9\times10^{-4} \pm 1\times10^{-4}$
MAE	$(NH_4)_2SO_4 + H_2SO_4$	0.03	2.78	$5.2\times10^{-4} \pm 1.1\times10^{-4}$

γ values are consistent with those measured in a previous study [Gaston et al., 2014, *ES&T*] and with aqueous phase reaction mechanisms [Eddingsaas et al., 2010, *JPCA*) – dependence on $[H^+]$, $[HSO_4^-]$, [nucleophile], but $[H^+]$ found to have strongest effect

[Riedel et al., 2015, *ES&T Letters*]

Modeling Smog Chamber Data

Chamber model setup:

- 0-D time-dependent chemical box model
- Initialize model with:
  - γ from flow reactor measurements
  - epoxide mass injected from chamber measurements
  - DMA reported aerosol [surface area] and [mass] from chamber measurements
- Only epoxide losses are to particles and chamber walls
- Only particle losses are to chamber walls

Modeling Smog Chamber Data

Chamber model setup:

- 0-D time-dependent chemical box model
- Initialize model with:
  - γ from flow reactor measurements
  - epoxide mass injected from chamber measurements
  - DMA reported aerosol [surface area] and [mass] from chamber measurements
- Only epoxide losses are to particles (makes SOA) and chamber walls
- Only particle losses are to chamber walls
- SOA production in the model:

$$P_{SOA} = \gamma \frac{S_a \omega}{4} \phi_{SOA} [epoxide]_{(g)}$$

[Riedel et al., 2015, *ES&T Letters*]

$$IEPOX_{(aq)} + H^+ + H_2O \rightarrow 2\text{-}methytetrols + H^+ \quad \text{(R1)}$$

$$IEPOX_{(aq)} + HSO_4^- + H_2O \rightarrow 2\text{-}methytetrols + H^+ + SO_4^{2-} \quad \text{(R2)}$$

$$IEPOX_{(aq)} + H^+ + SO_4^{2-} \rightarrow IEPOX\text{-}organosulfate + H^+ \quad \text{(R3)}$$

$$IEPOX_{(aq)} + HSO_4^- + SO_4^{2-} \rightarrow IEPOX\text{-}organosulfate + H^+ \quad \text{(R4)}$$

$$IEPOX_{(aq)} + H^+ \rightarrow C_5\text{-alkene triols} + H^+ \quad \text{(R5)}$$

$$IEPOX_{(aq)} + H^+ \rightarrow \text{3-MeTHF-3,4-diols} + H^+ \quad \text{(R6)}$$

$$IEPOX_{(aq)} + H^+ + \text{2-methyltetrols} \rightarrow \text{IEPOX-dimer} + H^+ \quad \text{(R7)}$$

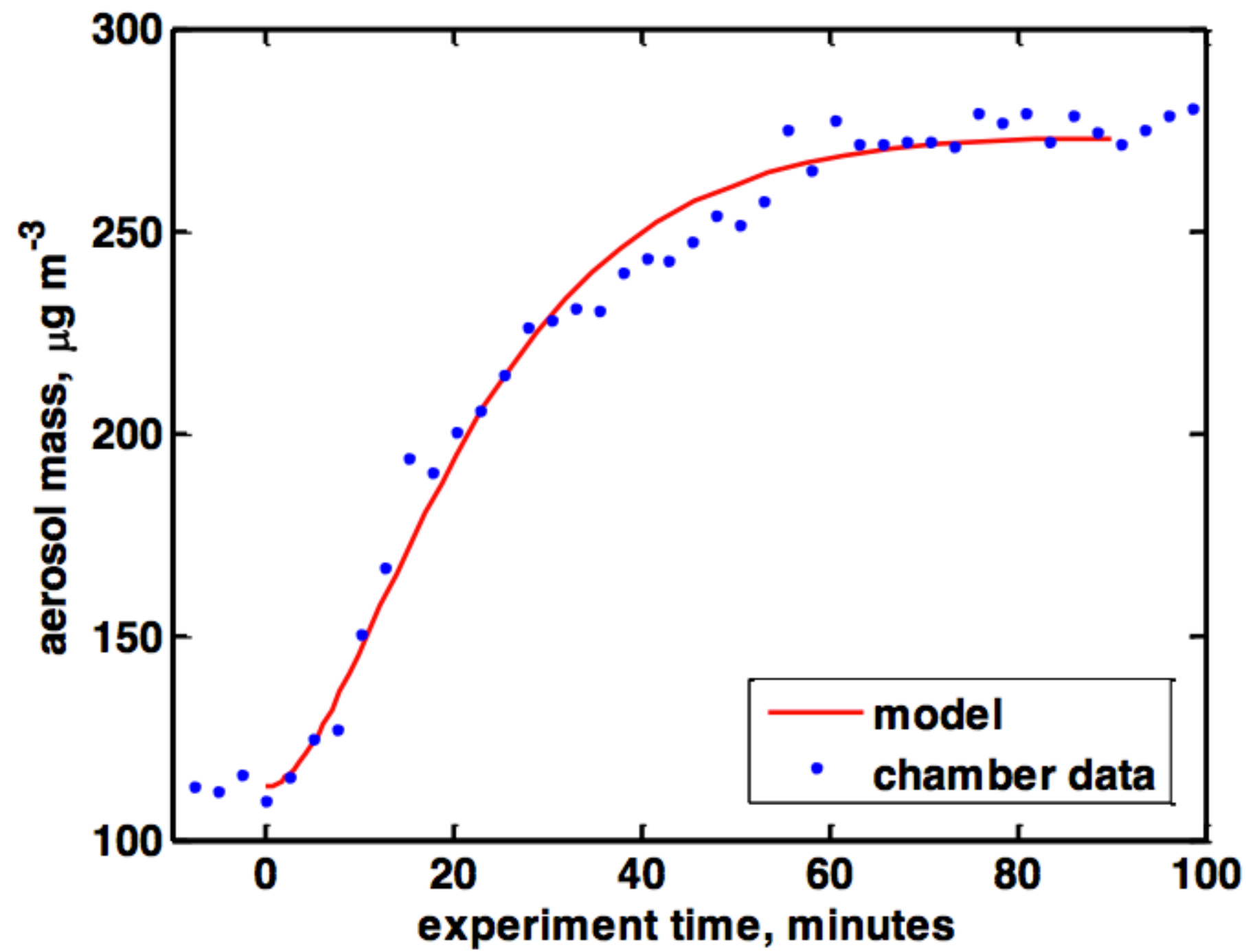
$$IEPOX_{(aq)} + H^+ + IEPOX\text{-OS} \rightarrow \text{IEPOX-dimerOS} + H^+ \quad \text{(R8)}$$

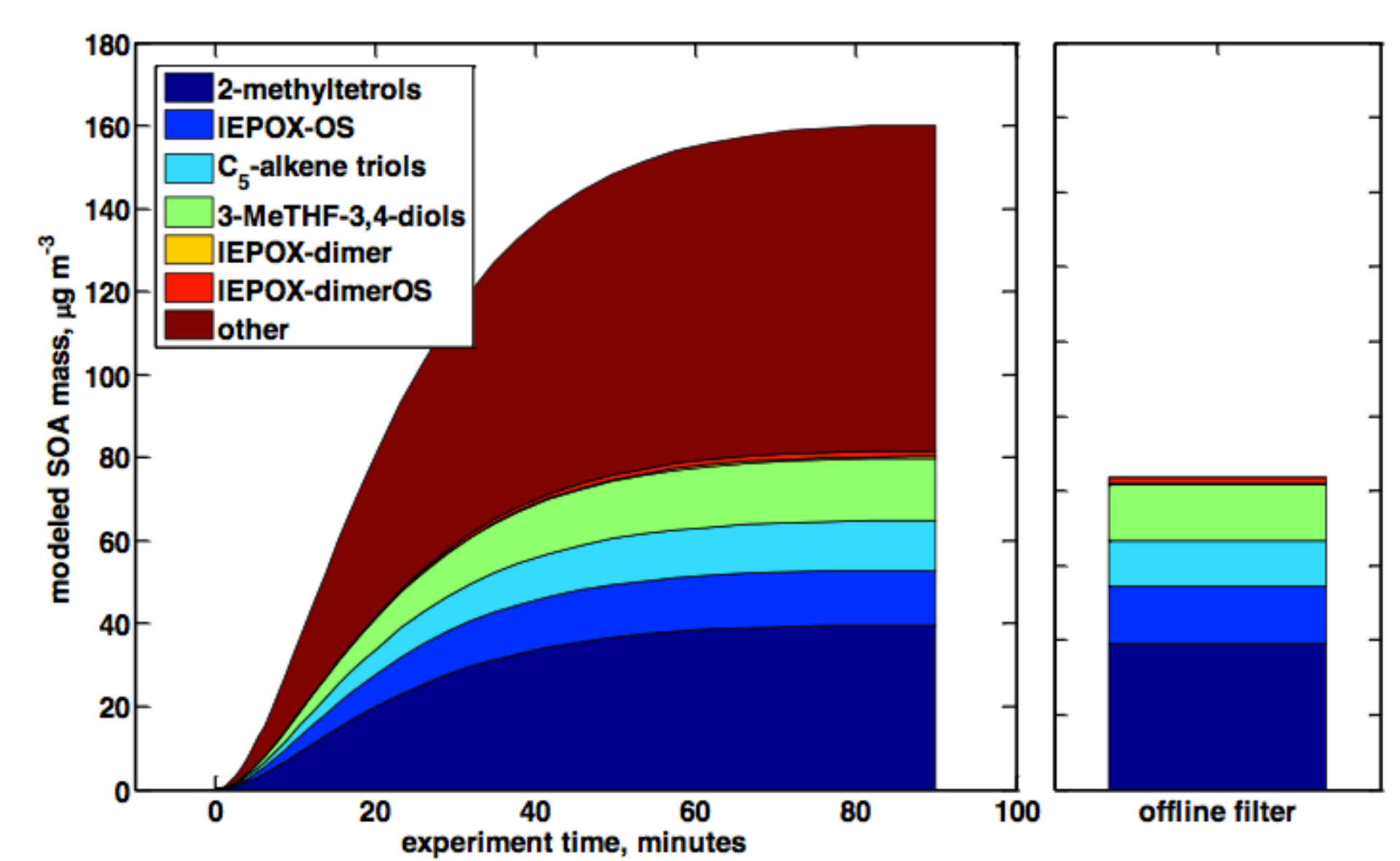
$$IEPOX_{(aq)} + H^+ \rightarrow \text{other SOA} + H^+ \quad \text{(R9)}$$

$$IEPOX_{(aq)} \rightarrow \text{volatile products} \quad \text{(R10)}$$

SOA tracer formed	k	reaction
2-methyltetrols	9.0×10^{-4} M^{-2} s [a]	(R1)
2-methyltetrols	1.3×10^{-5} M^{-2} s [a]	(R2)
IEPOX-OS	2.0×10^{-4} M^{-2} s [a]	(R3)
IEPOX-OS	2.9×10^{-6} M^{-2} s [a]	(R4)
C_5-alkene triols	$7.8 \pm 0.4 \times 10^{-4}$ M^{-1} s	(R5)
3-MeTHF-3,4-diols	$9.2 \pm 1.2 \times 10^{-4}$ M^{-1} s	(R6)
IEPOX-dimer	$7.7 \pm 2.7 \times 10^{-7}$ M^{-2} s	(R7)
IEPOX-dimerOS	$8.1 \pm 3.3 \times 10^{-6}$ M^{-2} s	(R8)
other SOA	$5.4 \pm 0.2 \times 10^{-3}$ M^{-1} s	(R9)

[a]from Eddingsaas et al., 2010; see also Pye et al., 2013


300
250
200
150
100
aerosol mass, μg m-3
0
20
40
60
80
100
experiment time, minutes
model
chamber data


2-methyltetrols
IEPOX-OS
C5-alkene triols
3-MeTHF-3,4-diols
IEPOX-dimer
IEPOX-dimerOS
other
modeled SOA mass, μg m-3
experiment time, minutes
offline filter
0
20
40
60
80
100
120
140
160
180

Questions?

www.unc.edu/~vizuete

Sensitivity Runs

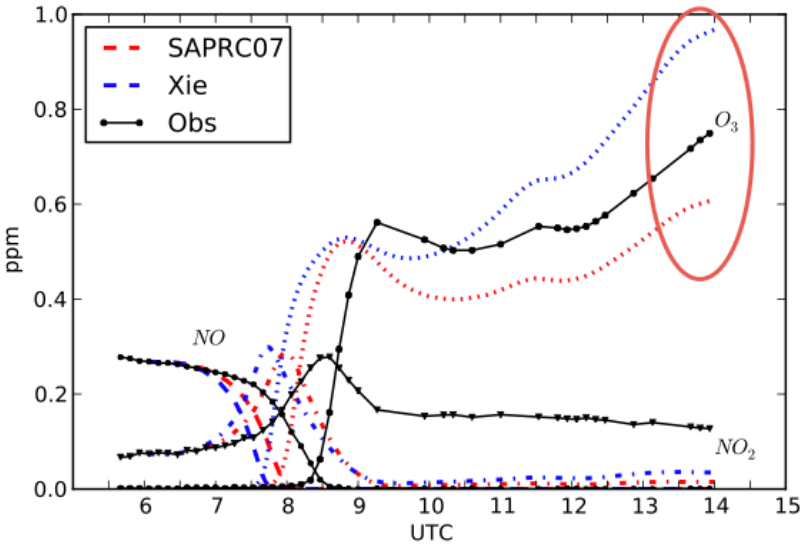
Lower NOX case: JN2697RED

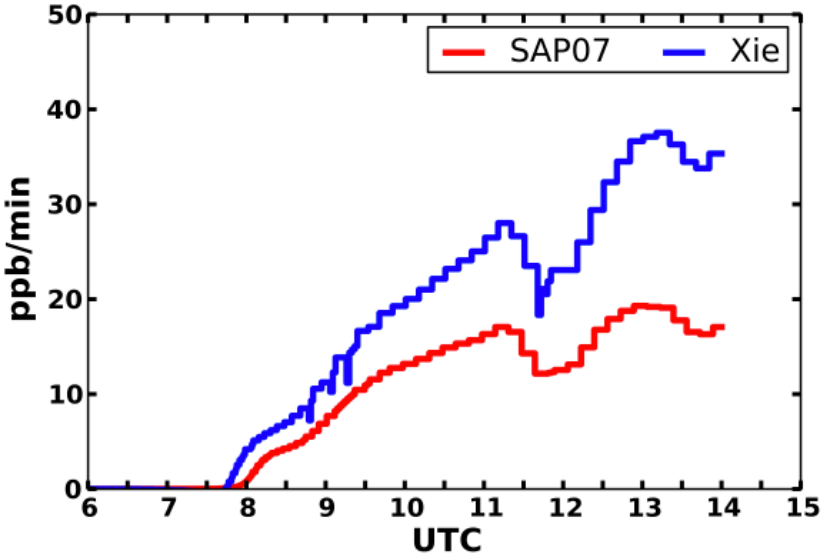
Case	Description	$K_{isom,ISOPO2}$	ISOPN yields
Run	BASE	K*	0.6
Run A	lower $K_{isom,ISOPO2}$	0.5K	0.6
Run B	lower ISOPN yield	K	0

*** K = (4.07e+8*EXP(-7694/TK) cm3/s**

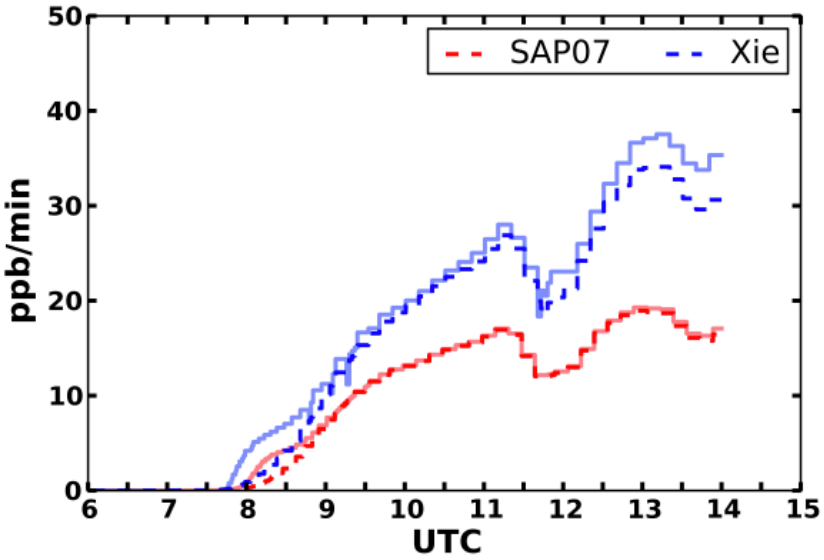
- ISOPO2 isomerization rate has no impacts on O_3
- ISOPN yields shut-down reduces O_3 maximum by 5%

NO_2 Recycling Rate





- PANs accounts for 92% of the total NO2 recycling from NOz
- Xie mechanism predicts 64% more PNA than SAPRC07



Radical Cycle for Lower NO_X Case

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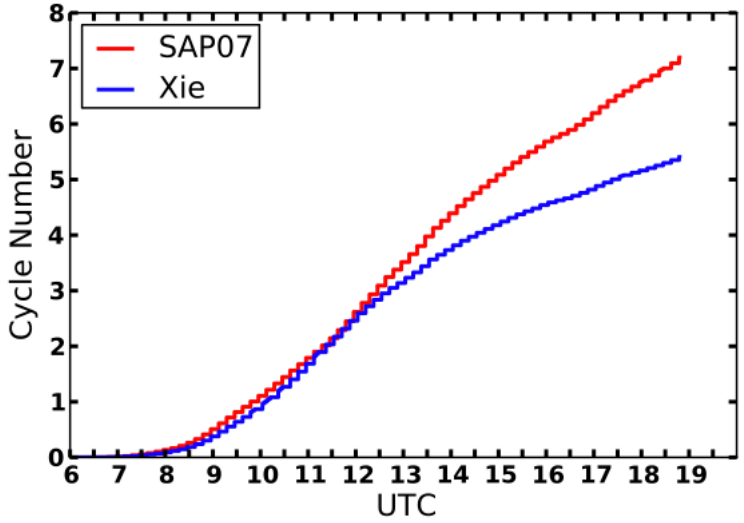
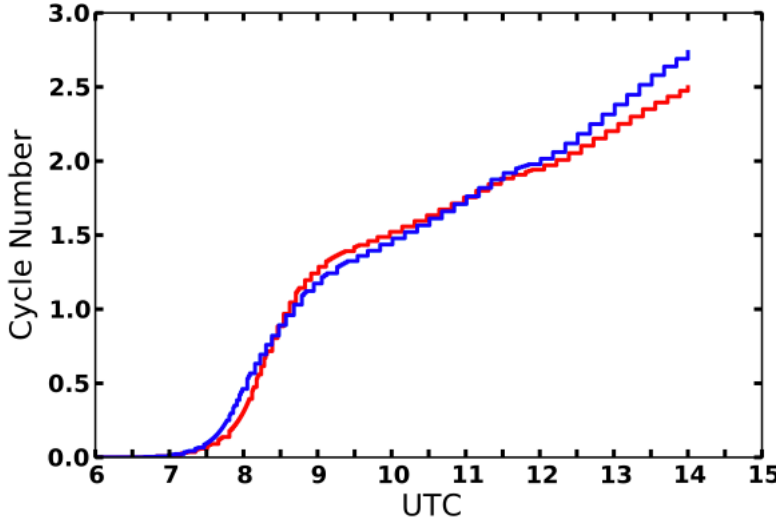
High NOx

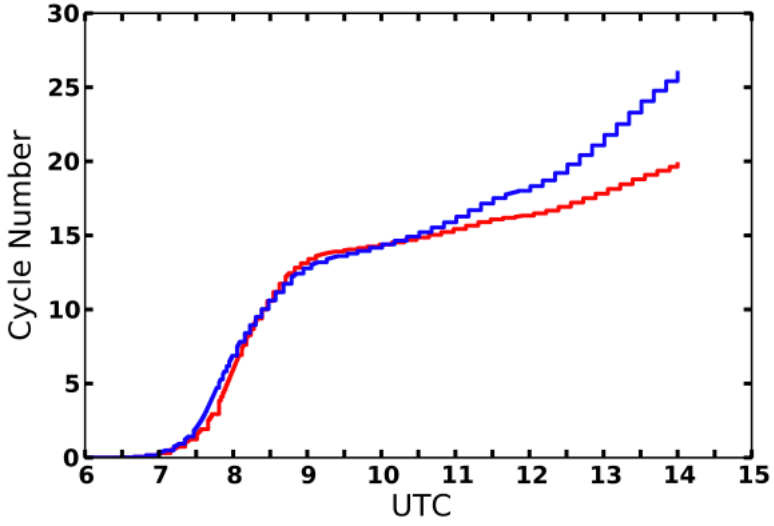
Lower NOx

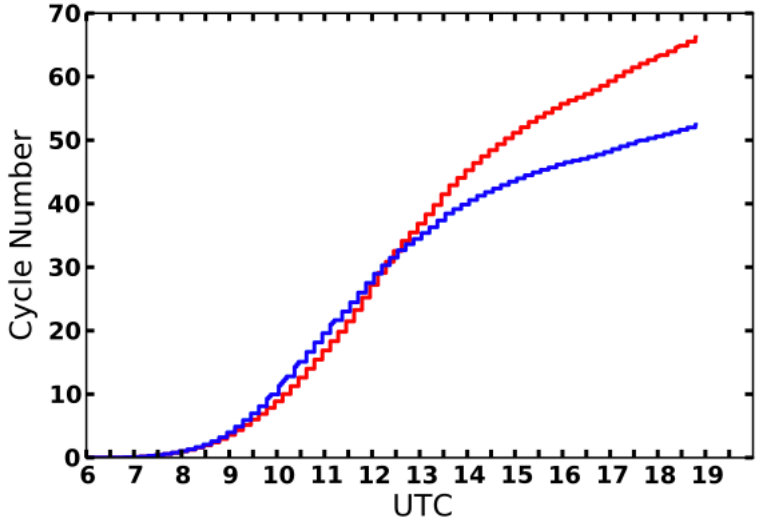
OH cycle





NO cycle





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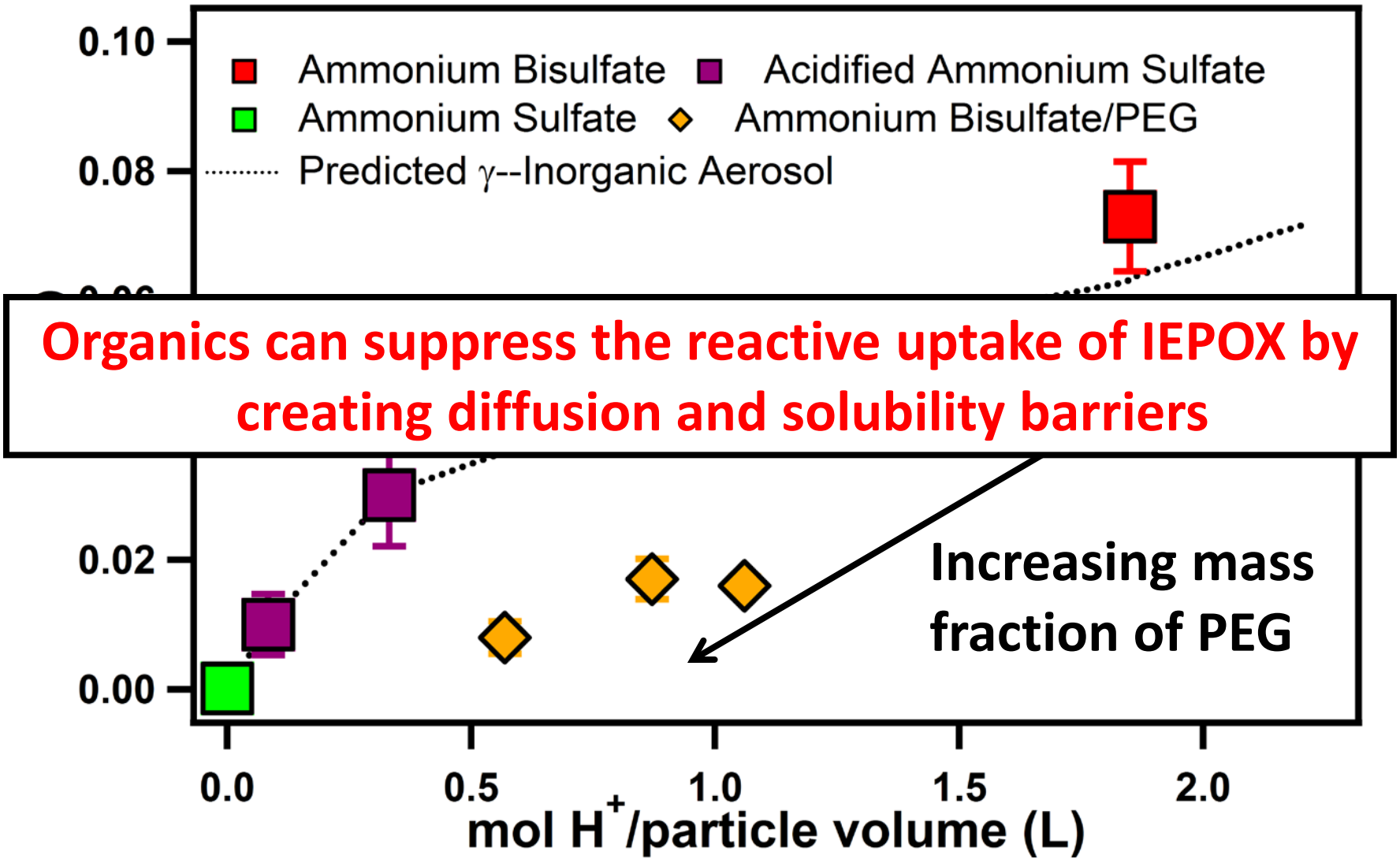
Do Organic Coatings Impact Uptake of IEPOX?



[Gaston et al., 2014, *ES&T*]

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ϕ_{SOA} Results

epoxide	aerosol	RH	aerosol $[H^+]$ (M)[a]	$\gamma \pm 1\sigma$	modeled ϕ_{SOA} range
IEPOX	$(NH_4)_2SO_4$	0.50	7.74×10^{-5}	$6.5\times10^{-4} \pm 6.4\times10^{-4}$	0.17 - 0.21
IEPOX	$MgSO_4 + H_2SO_4$	0.08	0.04	$1.1\times10^{-2} \pm 3\times10^{-3}$	0.04 - 0.06
IEPOX	$MgSO_4 + H_2SO_4$	0.53	0.73	$9.4\times10^{-3} \pm 3\times10^{-3}$	0.03 - 0.05
IEPOX	$(NH_4)_2SO_4 + H_2SO_4$	0.05	2.78	$2.1\times10^{-2} \pm 1\times10^{-3}$	0.10 - 0.12
IEPOX	$(NH_4)_2SO_4 + H_2SO_4$	0.59	2.01	$1.9\times10^{-2} \pm 2\times10^{-3}$	0.06 - 0.08
MAE	$MgSO_4 + H_2SO_4$	0.03	0.73	$4.9\times10^{-4} \pm 1\times10^{-4}$	0.07 - 0.14
MAE	$(NH_4)_2SO_4 + H_2SO_4$	0.03	2.78	$5.2\times10^{-4} \pm 1.1\times10^{-4}$	0.16 - 0.25

- **ϕ_{SOA} ranges 0.03 – 0.21 for IEPOX**
- **ϕ_{SOA} ranges 0.07 – 0.25 for MAE**
- **observed higher ϕ_{SOA} for $(NH_4)_2SO_4$ seed types**
- **similar ϕ_{SOA} for highly acidic and near neutral seed**
  - **SOA growth takes longer for near neutral seed**

[Riedel et al., 2015, *ES&T Letters*]

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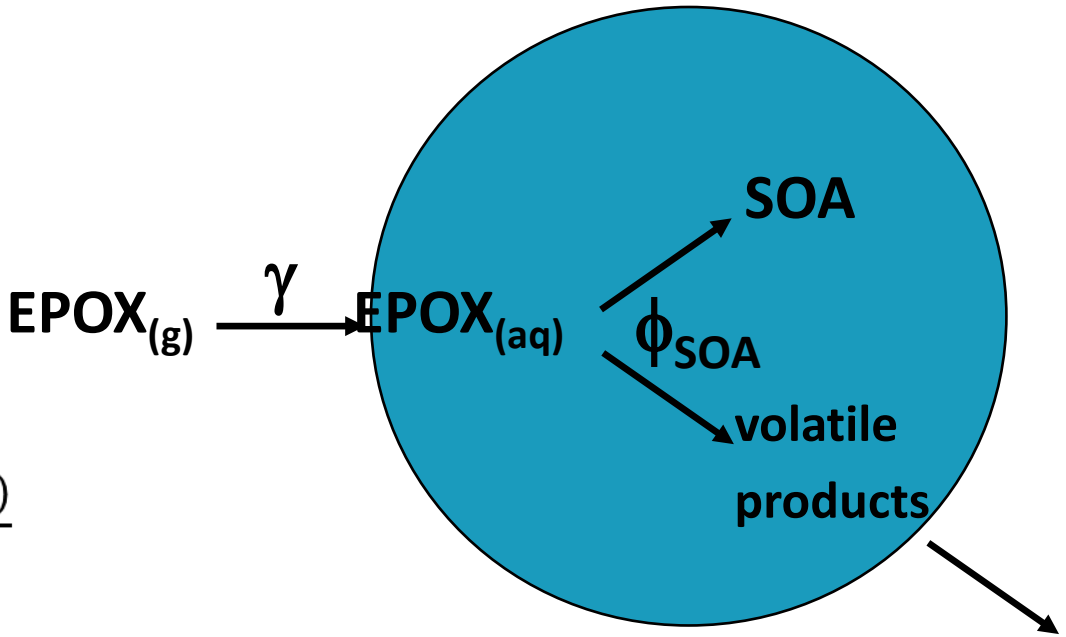
What Fraction Makes SOA?

$$SOA = tracer_1 + tracer_2 + tracer_i + \cdots tracer_n$$

$$SOA = organosulfate + 2 - methyltetrol + C_5\text{–}alkene\ triols + etc.$$



$$\phi_{SOA} = \frac{\sum_{i=1}^{n} k_i [epoxide]_{(aq)}}{k_{het}[epoxide]_{(g)}}$$

Can't quantify all tracers… so we need a different approach.

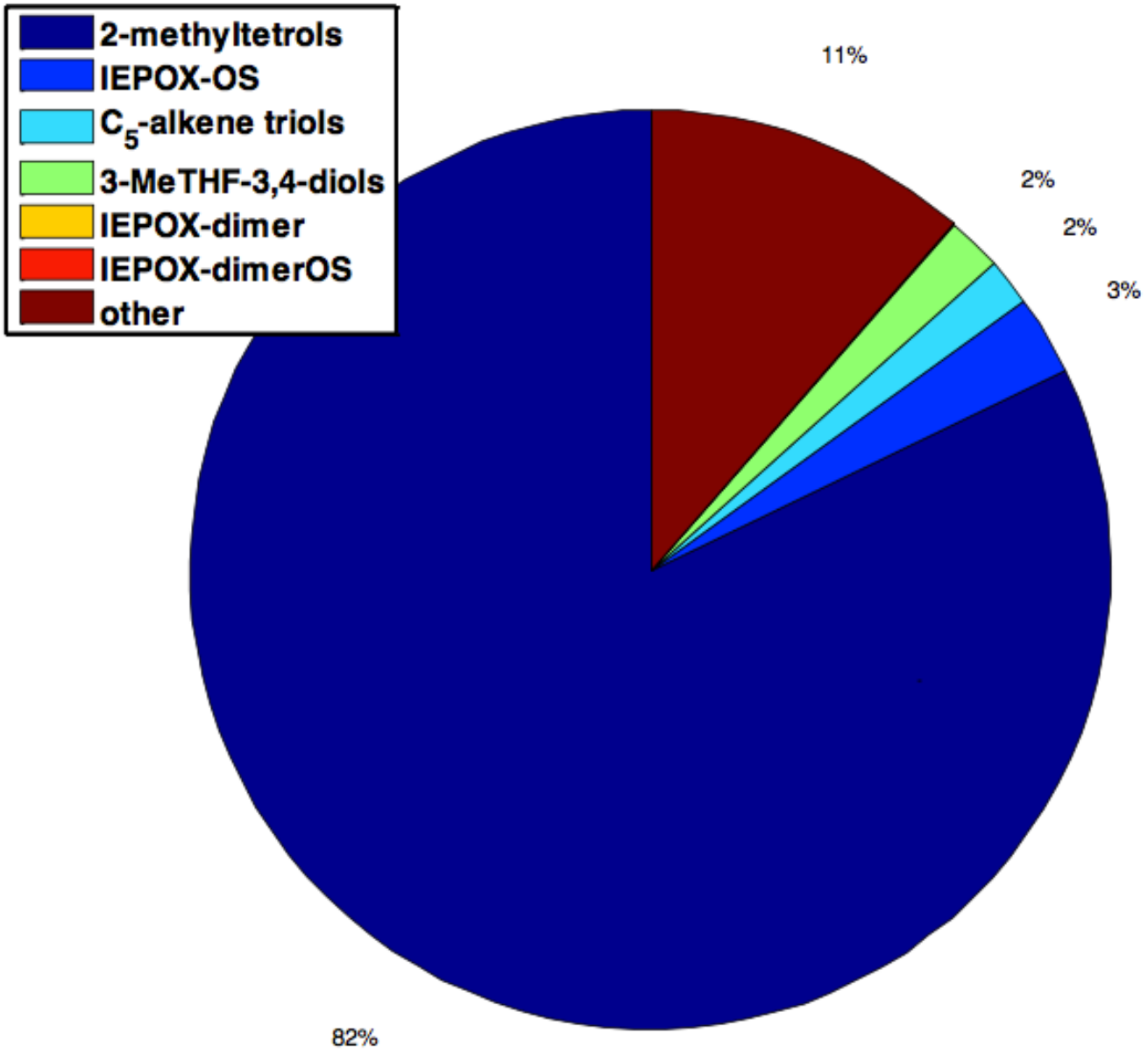
[Riedel et al., 2015, *ES&T Letters*]

In Conjunction with Existing Chamber Data, γ Results Used in Model to Estimate ϕ_{SOA}

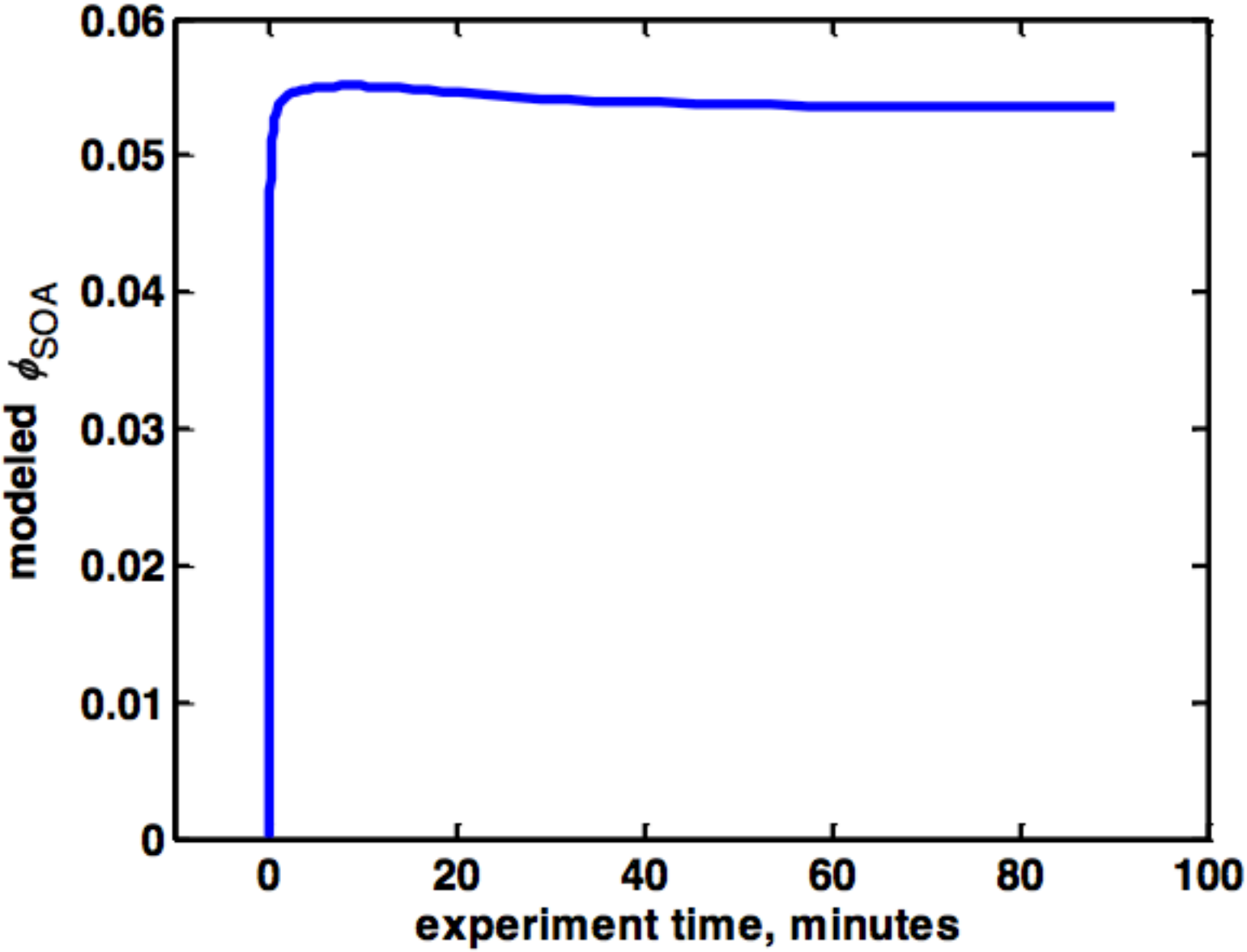
epoxide	aerosol	RH	aerosol $[H^+]$ (M)[a]	$\gamma \pm 1\sigma$
IEPOX	$(NH_4)_2SO_4$	0.50	7.74×10^{-5}	$6.5\times10^{-4} \pm 6.4\times10^{-4}$
IEPOX	$MgSO_4 + H_2SO_4$	0.08	0.04	$1.1\times10^{-2} \pm 3\times10^{-3}$
IEPOX	$MgSO_4 + H_2SO_4$	0.53	0.73	$9.4\times10^{-3} \pm 3\times10^{-3}$
IEPOX	$(NH_4)_2SO_4 + H_2SO_4$	0.05	2.78	$2.1\times10^{-2} \pm 1\times10^{-3}$
IEPOX	$(NH_4)_2SO_4 + H_2SO_4$	0.59	2.01	$1.9\times10^{-2} \pm 2\times10^{-3}$
MAE	$MgSO_4 + H_2SO_4$	0.03	0.73	$4.9\times10^{-4} \pm 1\times10^{-4}$
MAE	$(NH_4)_2SO_4 + H_2SO_4$	0.03	2.78	$5.2\times10^{-4} \pm 1.1\times10^{-4}$

Chosen to match aerosol composition and RH from chambers studies showing observable SOA production.

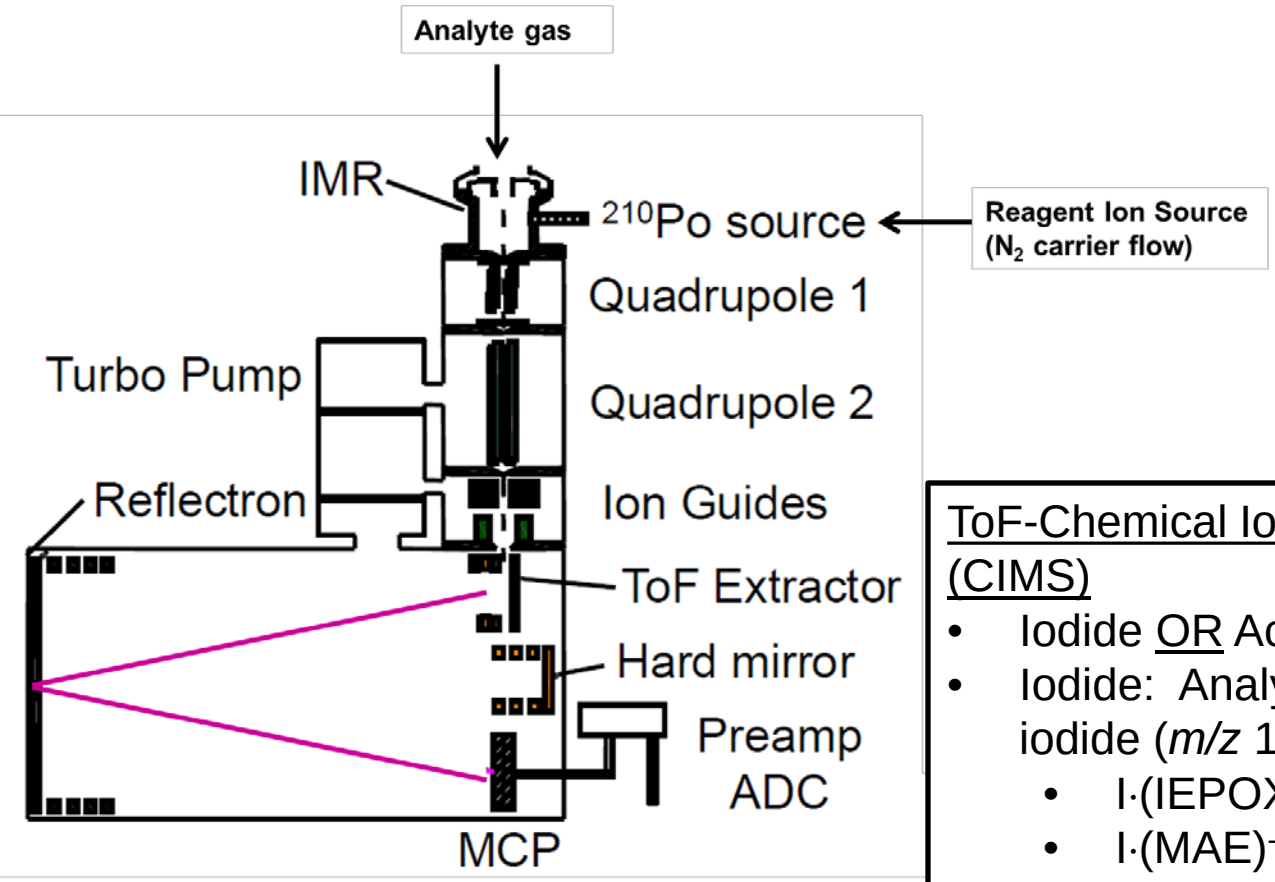
[Riedel et al., 2015, *ES&T Letters*]



Total predicted SOA mass = 0.45 μg m^{-3}


0.06
0.05
0.04
0.03
0.02
0.01
0
modeled ϕ_{SOA}
0
20
40
60
80
100
experiment time, minutes

Measuring Reactive Uptake



ToF-Chemical Ionziation Mass Spectrometer (CIMS)

- Iodide OR Acetate reagent chemistry
- Iodide: Analyte detected as cluster with iodide (*m/z* 126.9)
  - $I\cdot(IEPOX)^-$: *m/z* 244.9
  - $I\cdot(MAE)^-$: *m/z* 228.9
- Acetate: Analyte detected as cluster with acetate (m/z 59) or deprotonated acid
  - $C_2H_3O_2\cdot(IEPOX)^-$: *m/z* 177 (cluster)
  - $MAE(-H^+)$: *m/z* 101 (deprotonated)