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Impacts of Anthropogenic Emissions in the Southeastern U.S. on Heterogeneous Chemistry of Isoprene-Derived Epoxides Leading to Secondary Organic Aerosol Formation

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U.S. EPA STAR Progress Review Meeting: Anthropogenic Influences on Organic Aerosol Formation and Regional Climate Implications

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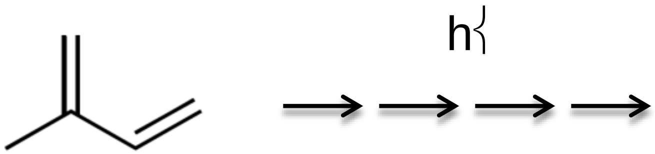
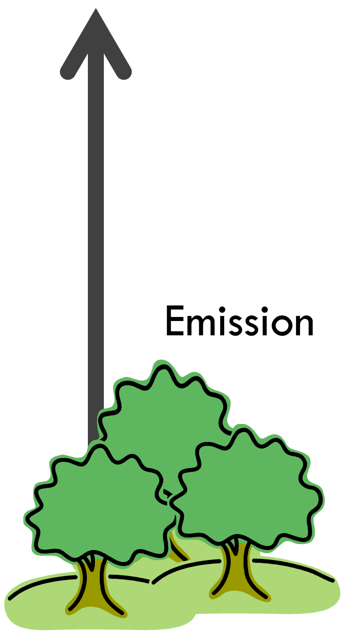
Brief History of Isoprene SOA – Need for Chemical Characterization & Proper Reaction Conditions



isoprene

Oxidants
(OH, O_3)

Negligible SOA formed, even at HIGH isoprene mixing ratios!



Emission

Ozone–Isoprene Reactions: Product Formation and Aerosol Potential

R. M. KAMENS, M. W. GERY, H. E. JEFFRIES, M. JACKSON, and E. I. COLE

Department of Environmental Sciences and Engineering, School of Public Health, University of North Carolina, Chapel Hill, North Carolina 27514, U.S.A.

Kamens et al., *Int. J Chem. Kinet.* (1982)

AEROSOL FORMATION IN THE PHOTOOXIDATION OF ISOPRENE AND β-PINENE

SPYROS N. PANDIS,* SUZANNE E. PAULSON,† JOHN H. SEINFELD* and RICHARD C. FLAGAN*

*Department of Chemical Engineering and †Department of Environmental Engineering Science, California Institute of Technology, Pasadena, CA 91125, U.S.A.

(*First received 29 May 1990 and in final form 4 September* 1990)

Pandis et al., *Atmos. Environ.* (1991)

CHARACTERIZATION OF PHOTOCHEMICAL AEROSOLS FROM BIOGENIC HYDROCARBONS

S. E. PAULSON, S. N. PANDIS, U. BALTENSPERGER, J. H. SEINFELD, R. C. FLAGAN
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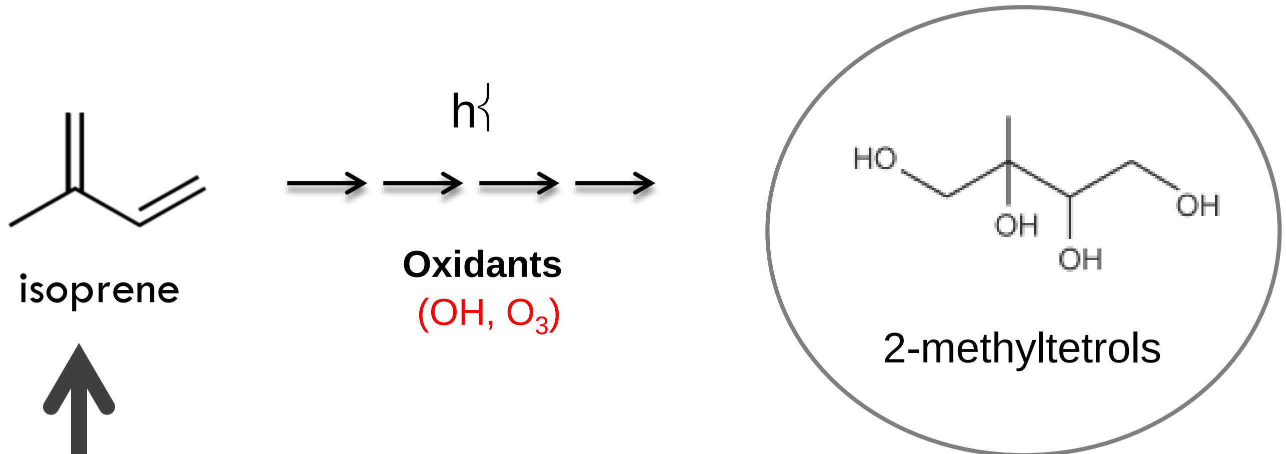
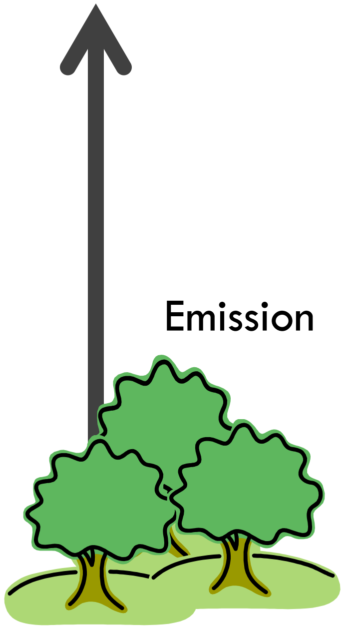
Paulson et al., *J. Aerosol Sci.* (1990)

Brief History of Isoprene SOA Formation – Importance of Chemical Characterization



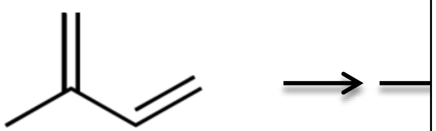


Formation of Secondary Organic Aerosols Through Photooxidation of Isoprene

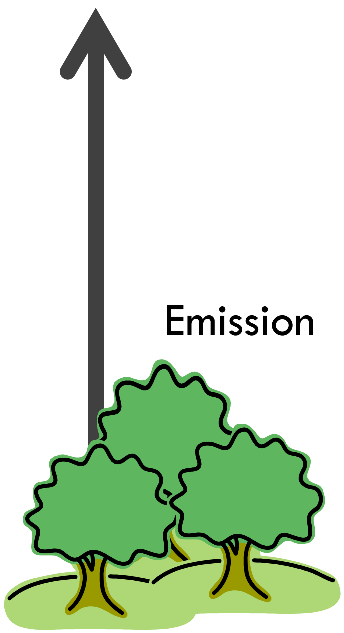
Magda Claeys,[1]* Bim Graham,[2,3] Gyorgy Vas,[1] Wu Wang,[1] Reinhilde Vermeylen,[1] Vlada Pashynska,[1] Jan Cafmeyer,[4] Pascal Guyon,[2] Meinrat O. Andreae,[2] Paulo Artaxo,[5] Willy Maenhaut[4]

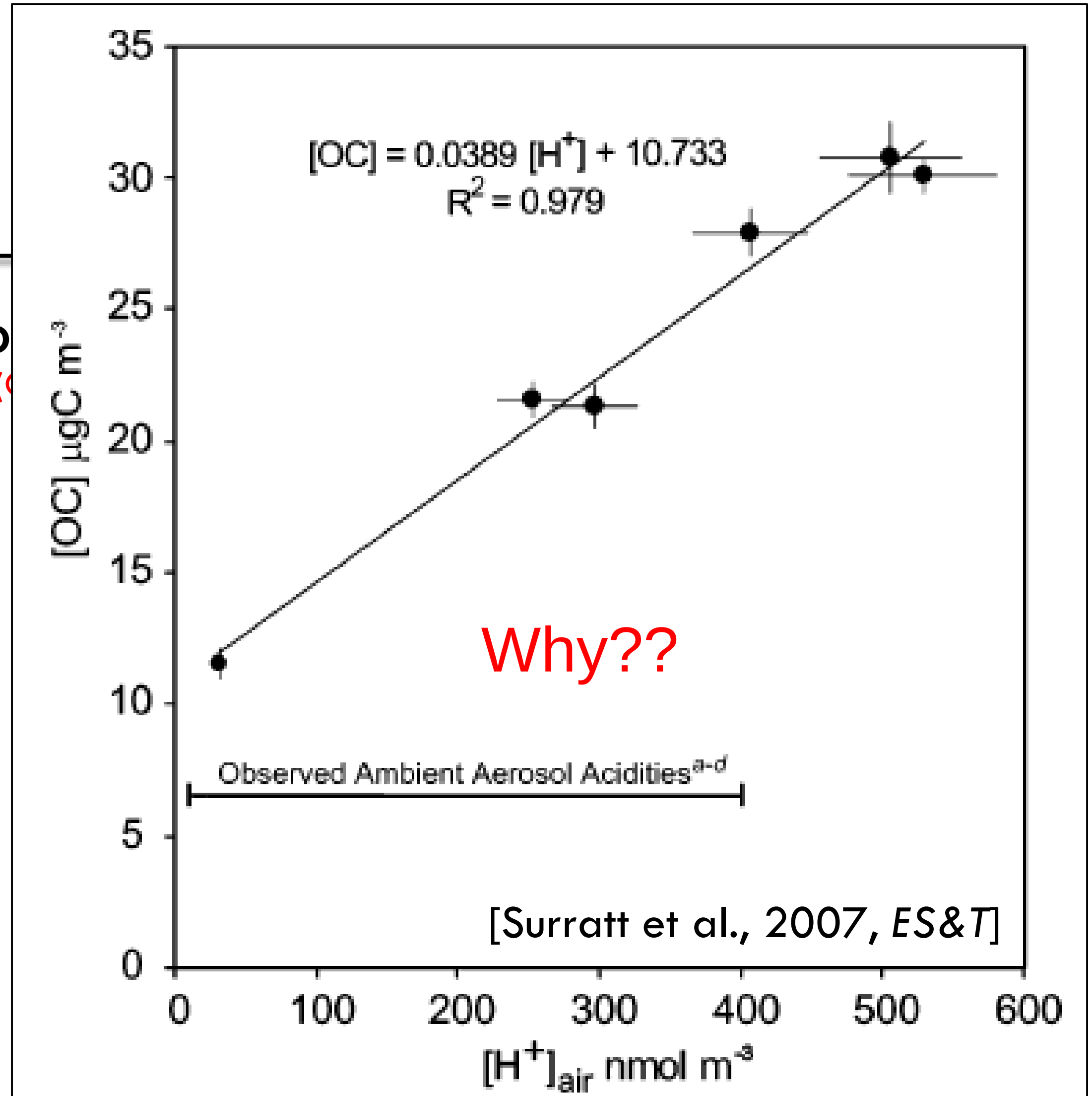
Claeys et al., *Science* (2004)

Anthropogenic Pollutants Enhance Isoprene SOA – Need for Understanding Rxn Conditions



isoprene





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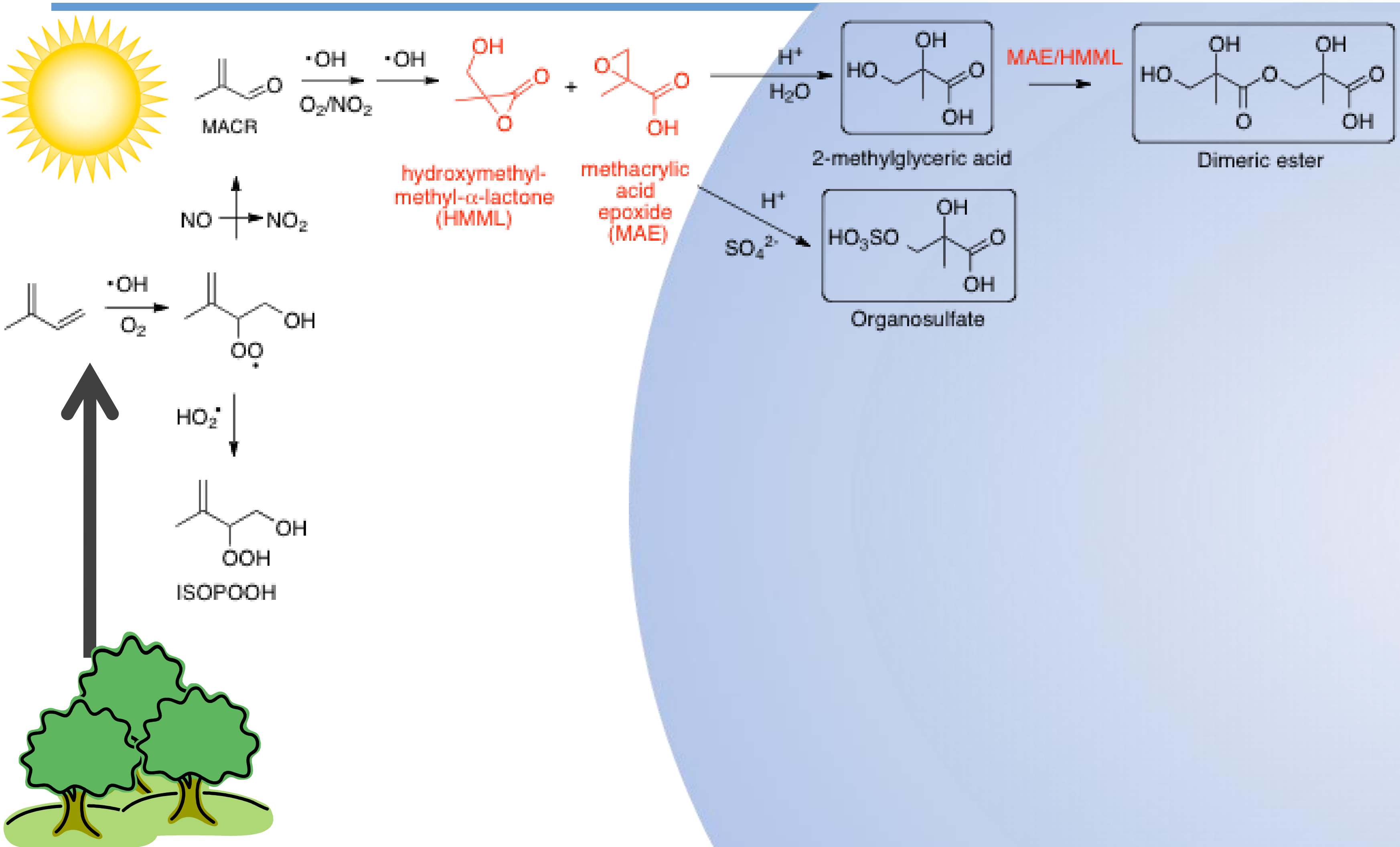
Multiphase Chemistry of Isoprene-Derived Oxidation Products Promote SOA Formation



[Kroll et al., 2006; Surratt et al., 2006; Surratt et al., 2010, Chan et al., 2010; Zhang et al., 2011; Lin et al., 2013; Lin et al., 2013; Riedel et al., 2015; Nguyen et al.,

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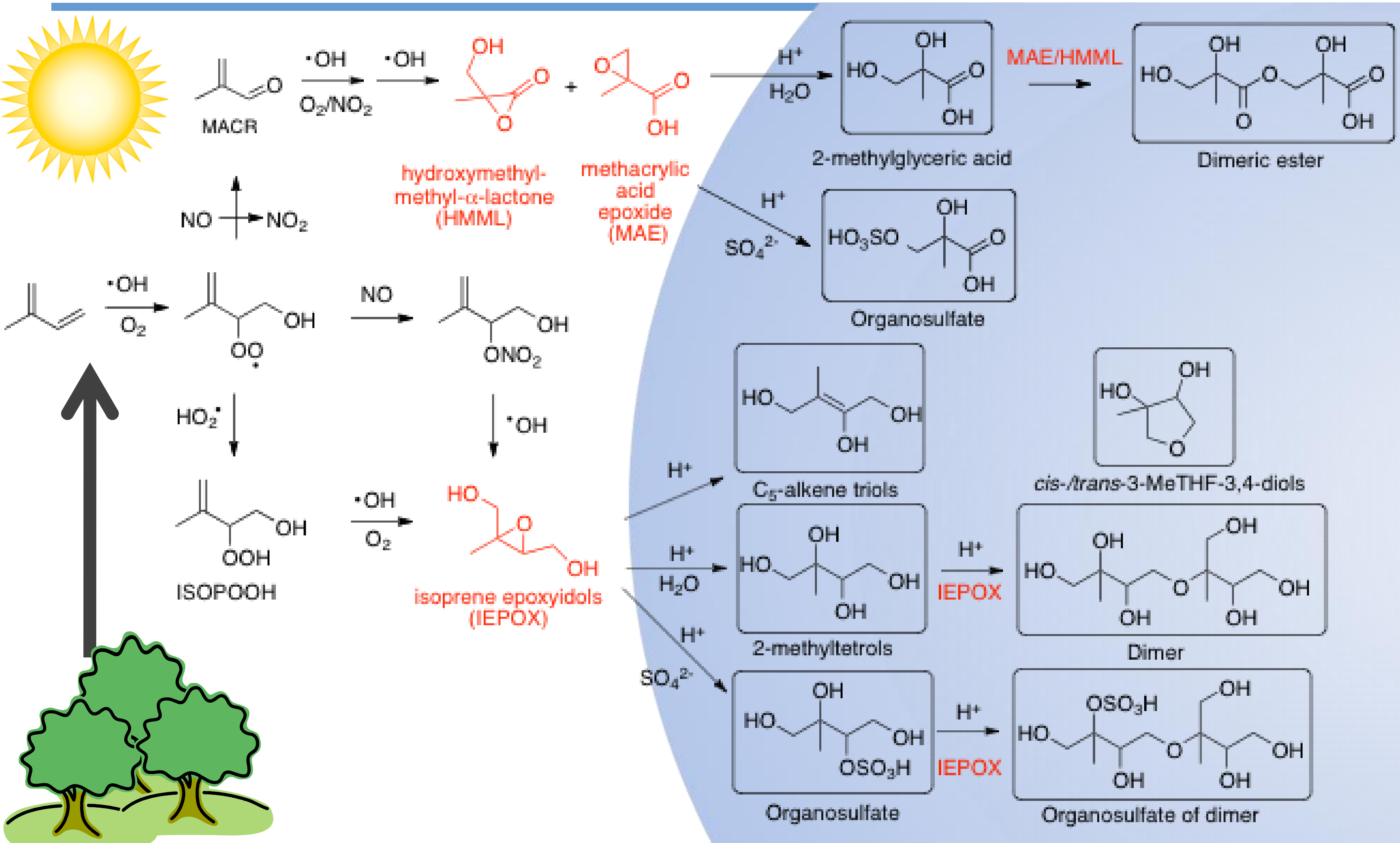

[Paulot et al., 2009; Surratt et al., 2010, Lin et al., 2012; Lin et al., 2013; Lin et al., 2014; Nguyen et al., 2014; Jacobs et al., 2014; Gaston et al., 2014; Riedel et al., 2015; Liu et al., 2016]

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Research Questions My Group & Collaborators Addressed During Project Period

- Do you **anthropogenic pollutants** alter isoprene SOA formation in the S.E. USA through multiphase chemistry of epoxides?

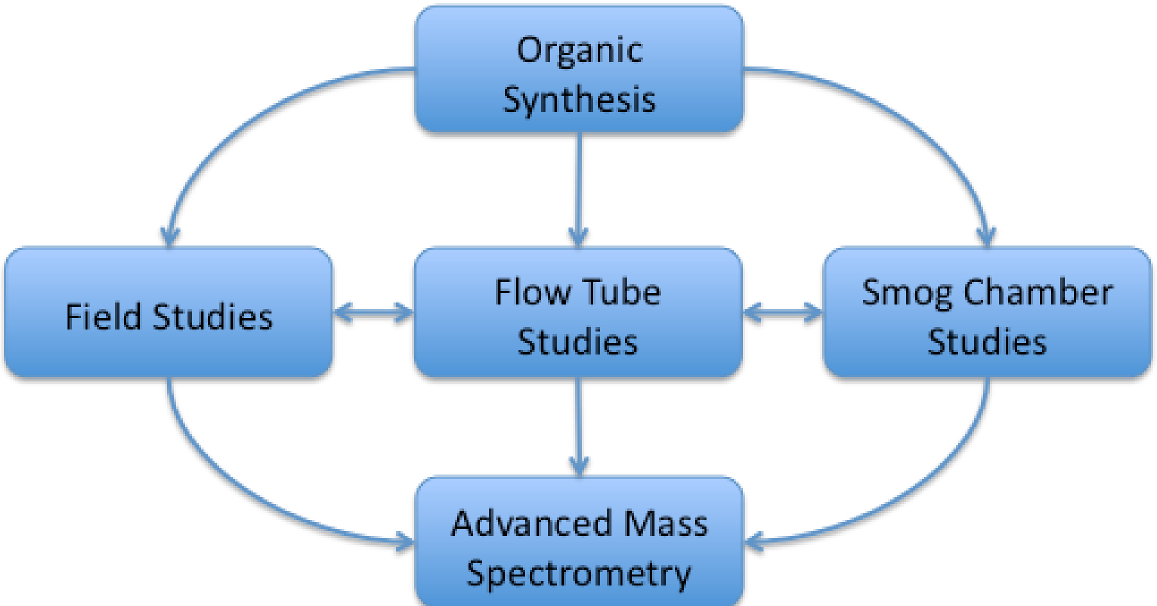
- What are spatial (urban vs. rural) & temporal variations of isoprene SOA in S.E. USA?

- Do light-absorbing (**brown carbon**) constituents form from multiphase chemistry of isoprene-derived epoxides?

- What are the uptake kinetics of isoprene-derived epoxides & do SOA coatings/ mixtures have an effect?

- Can model predictions of isoprene SOA match chamber data? If so, how about about field observations (collaborative work with McNeill, Pye, & Nenes)?

My Group's Current Research Approach



Expected Results: Derive parameterizations needed for improving atmospheric modeling of isoprene-derived SOA enhanced due to presence of anthropogenic pollutants

Implications: True impact of isoprene-derived SOA on air quality, regional and global climate, and human health can be more fully assessed

UNC 120-m^3 Gillings Outdoor Smog Chamber

UNC 274-m^3 Dual Outdoor Smog Chamber

UNC 10-m^3 Indoor Smog Chamber

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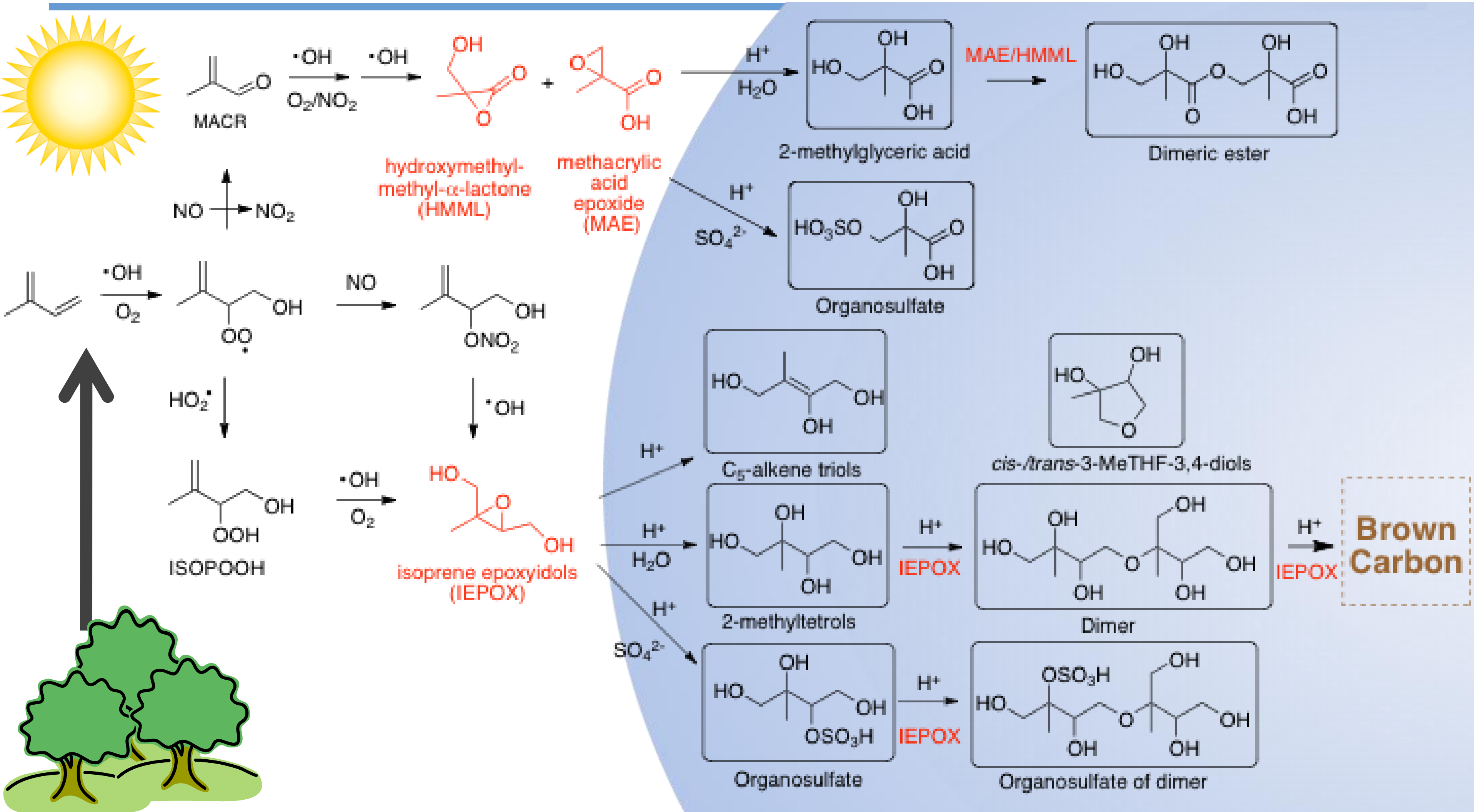
Multiphase Chemistry of Isoprene-Derived Oxidation Products Promote SOA Formation



[Lin et al., 2014; Nakayama et al., 2015]

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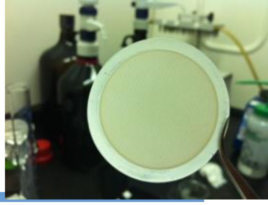
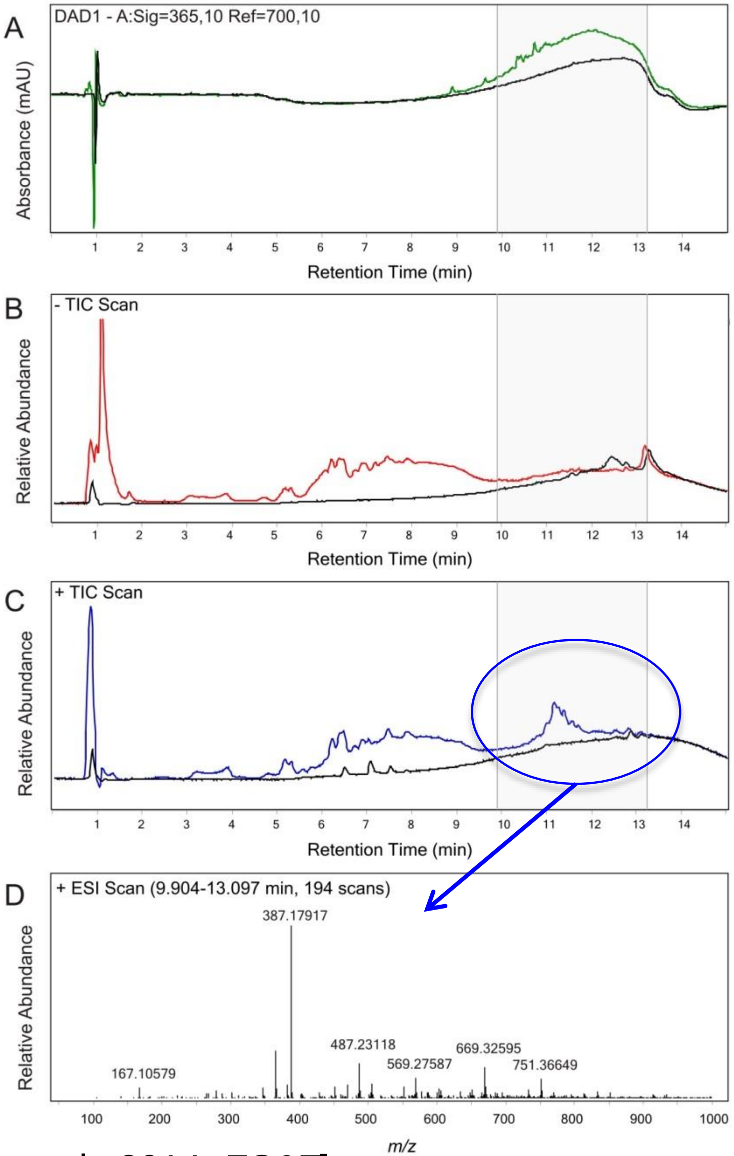
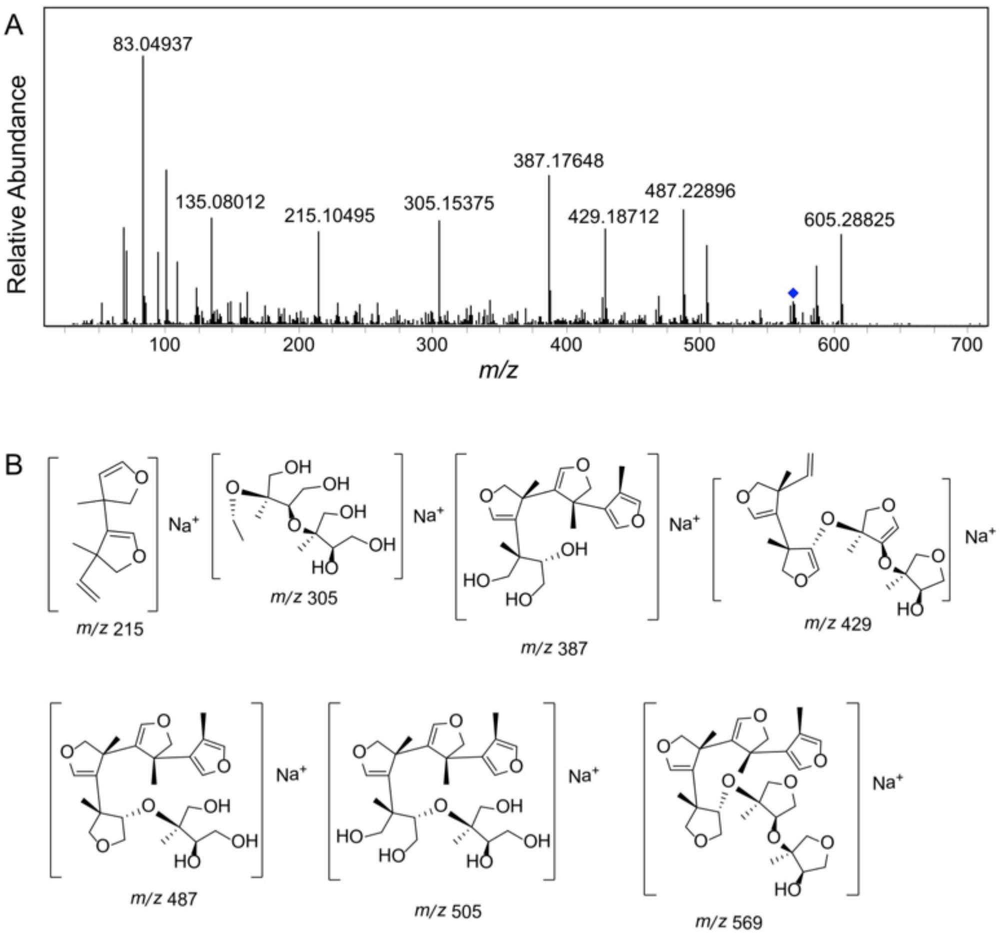
Chemical Characterization of Brown Carbon Oligomers From IEPOX





Tandem MS[2] of *m/z* 569 (10 DBE Oligomer):



Note that *m/z* 83 is protonated 3-methylfuran

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

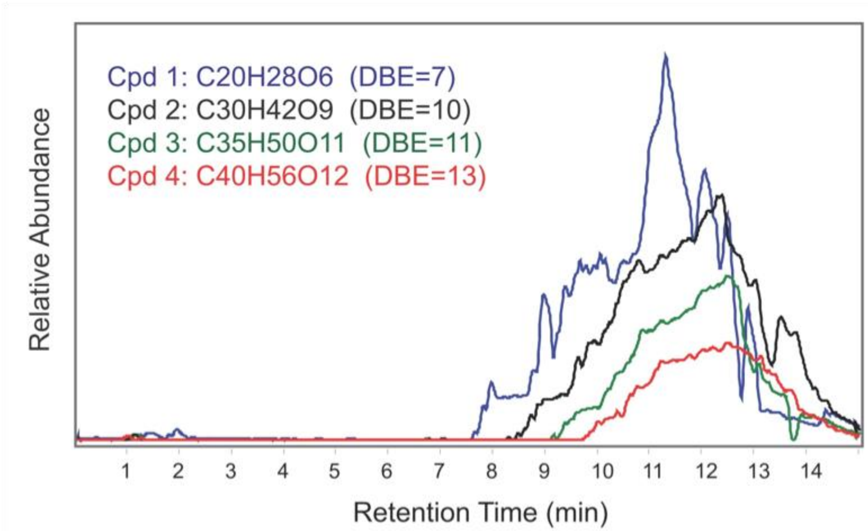
Non-Brown Carbon & Brown Carbon Oligomers Observed in 2013 SOAS Samples

Measured *m/z*	Ion	Proposed formula	Theoretical *m/z*	Diff (mDa)	DBE
Retention time: 5 – 8 min					
137.08072	(M+H)+	$C_5H_{12}O_4$	137.08084	0.12	0
237.13316	(M+H)+	$C_{10}H_{20}O_6$	237.13326	0.11	1
255.14415	(M+H)+	$C_{10}H_{22}O_7$	255.14383	-0.32	0
259.11587	(M+Na)+	$C_{10}H_{20}O_6$	259.11521	-0.66	1
277.12636	(M+Na)+	$C_{10}H_{22}O_7$	277.12577	-0.59	0
355.19653	(M+H)+	$C_{15}H_{30}O_9$	355.19626	-0.27	1
359.16765	(M+Na)+	$C_{15}H_{28}O_8$	359.16764	-0.01	2
373.20717	(M+H)+	$C_{15}H_{32}O_{10}$	373.20682	-0.35	0
377.17919	(M+Na)+	$C_{15}H_{30}O_9$	377.1782	-0.98	1
395.18987	(M+Na)+	$C_{15}H_{32}O_{10}$	395.18877	-1.10	0
473.25933	(M+H)+	$C_{20}H_{40}O_{12}$	473.25925	-0.06	1
477.23059	(M+Na)+	$C_{20}H_{38}O_{11}$	477.23063	0.05	2
491.27000	(M+H)+	$C_{20}H_{42}O_{13}$	491.26982	-0.17	0
495.24214	(M+Na)+	$C_{20}H_{40}O_{12}$	495.2412	-0.93	1
513.25261	(M+Na)+	$C_{20}H_{42}O_{13}$	513.25176	-0.84	0
613.30012	(M+Na)+	$C_{25}H_{50}O_{15}$	613.30419	4.08	1
631.31453	(M+Na)+	$C_{25}H_{52}O_{16}$	631.31476	0.24	0
727.39423	(M+H)+	$C_{30}H_{62}O_{19}$	727.39581	1.62	0
731.36577	(M+Na)+	$C_{30}H_{60}O_{18}$	731.36719	1.45	1
749.37624	(M+Na)+	$C_{30}H_{62}O_{19}$	749.37775	1.53	0
Retention time: 9– 14 min					
167.10610	(M+H)+	$C_{10}H_{14}O_2$	167.10666	0.56	4
267.16135	(M+H)+	$C_{15}H_{22}O_4$	267.15909	-2.26	5
347.18495	(M+H)+	$C_{20}H_{26}O_5$	347.18530	0.35	8
365.19608	(M+H)+	$C_{20}H_{28}O_6$	365.19587	-0.21	7
387.17895	(M+Na)+	$C_{20}H_{28}O_6$	387.17781	-1.14	7
451.20949	(M+Na)+	$C_{25}H_{32}O_6$	451.20911	-0.38	10
469.21771	(M+Na)+	$C_{25}H_{34}O_7$	469.21967	1.96	9
487.23083	(M+Na)+	$C_{25}H_{36}O_8$	487.23024	-0.59	8
505.24069	(M+Na)+	$C_{25}H_{38}O_9$	505.24080	0.11	7
547.28908	(M+H)+	$C_{30}H_{42}O_9$	547.29016	1.08	10
569.27281	(M+Na)+	$C_{30}H_{42}O_9$	569.27210	-0.71	10
647.34255	(M+H)+	$C_{35}H_{50}O_{11}$	647.34259	0.04	11
669.32510	(M+Na)+	$C_{35}H_{50}O_{11}$	669.32453	-0.57	11
733.35478	(M+Na)+	$C_{40}H_{54}O_{11}$	733.35583	1.05	14
751.36618	(M+Na)+	$C_{40}H_{56}O_{12}$	751.36640	0.22	13
769.37637	(M+Na)+	$C_{40}H_{58}O_{13}$	769.37696	0.59	12
833.40590	(M+Na)+	$C_{45}H_{62}O_{13}$	833.40826	2.36	15
851.41803	(M+Na)+	$C_{45}H_{64}O_{14}$	851.41883	0.80	14
933.46009	(M+Na)+	$C_{50}H_{70}O_{15}$	933.46059	0.50	16
951.46835	(M+Na)+	$C_{50}H_{72}O_{16}$	951.47126	2.91	15

[Lin et al., 2014, ES&T]

Non-Brown Carbon Oligomers

Brown Carbon Oligomers in $PM_{2.5}$ from YRK, GA:



Non-Brown Carbon & Brown Carbon Oligomers Have Implications for Volatility of Isoprene SOA

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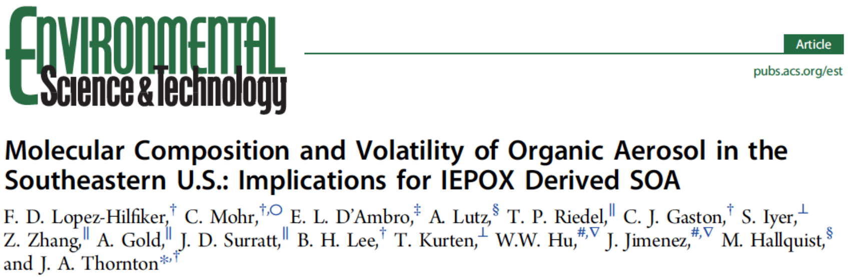
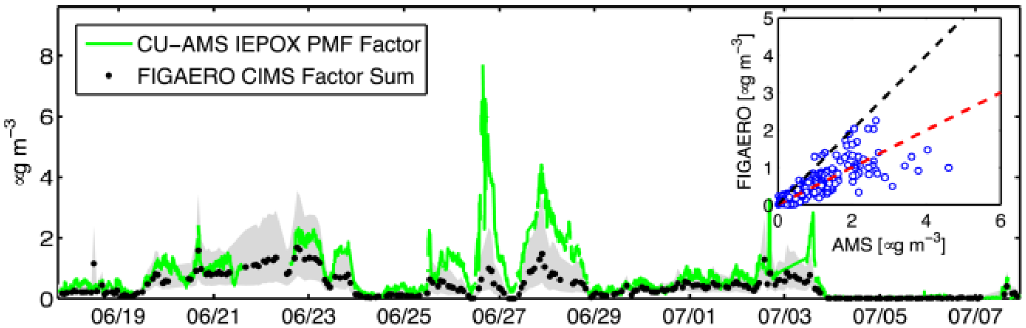
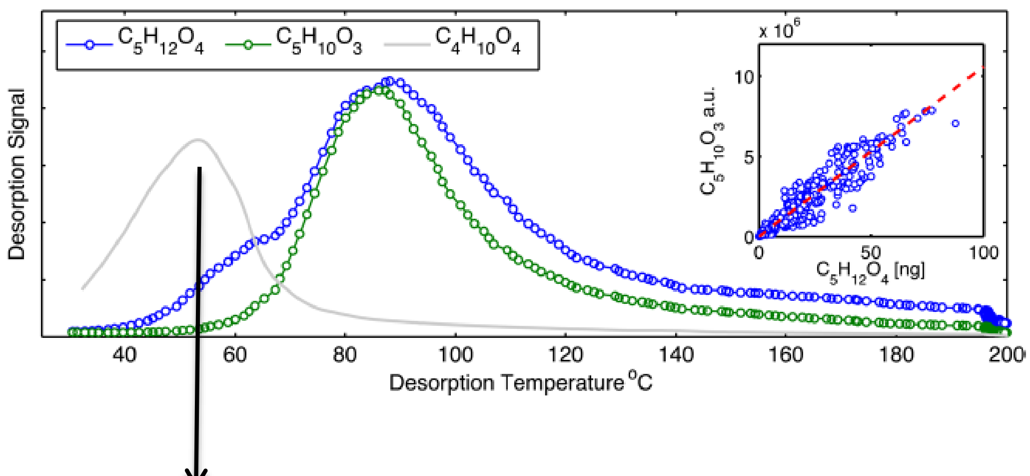

Environmental Science & Technology
Article
pubs.acs.org/est

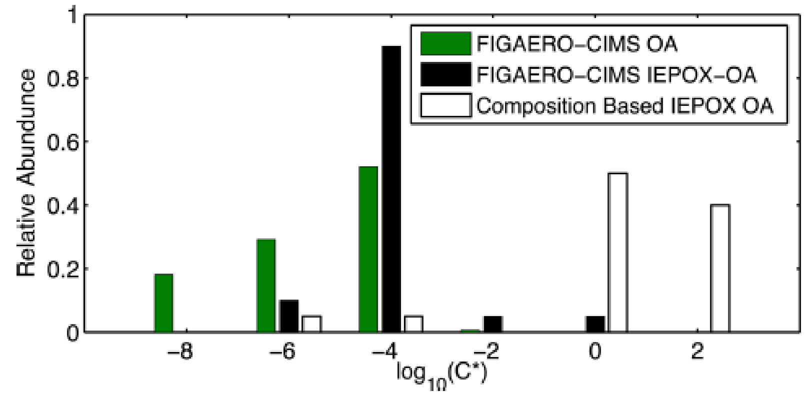
Molecular Composition and Volatility of Organic Aerosol in the Southeastern U.S.: Implications for IEPOX Derived SOA

F. D. Lopez-Hilfiker,[†] C. Mohr,[†,○] E. L. D'Ambro,[‡] A. Lutz,[§] T. P. Riedel,[∥] C. J. Gaston,[†] S. Iyer,[⊥] Z. Zhang,[∥] A. Gold,[∥] J. D. Surratt,[∥] B. H. Lee,[†] T. Kurten,[⊥] W.W. Hu,[#,∇] J. Jimenez,[#,∇] M. Hallquist,[§] and J. A. Thornton[*,†]





2-methyltetrol standard



<u>VBS</u>: Actual volatility of IEPOX-SOA measured by FIGAERO-CIMS (black bars) reveal *C more than 3 orders of magnitude lower than structure-activity estimates (white bars) of known IEPOX-SOA tracers**

FIGAERO-CIMS suggests that IEPOX-SOA is compromised of effectively non-volatile SOA, thus has implications for modeling!

Organic Synthesis of Gas- and Aerosol-Phase Products Has Helped to Confirm Pathways

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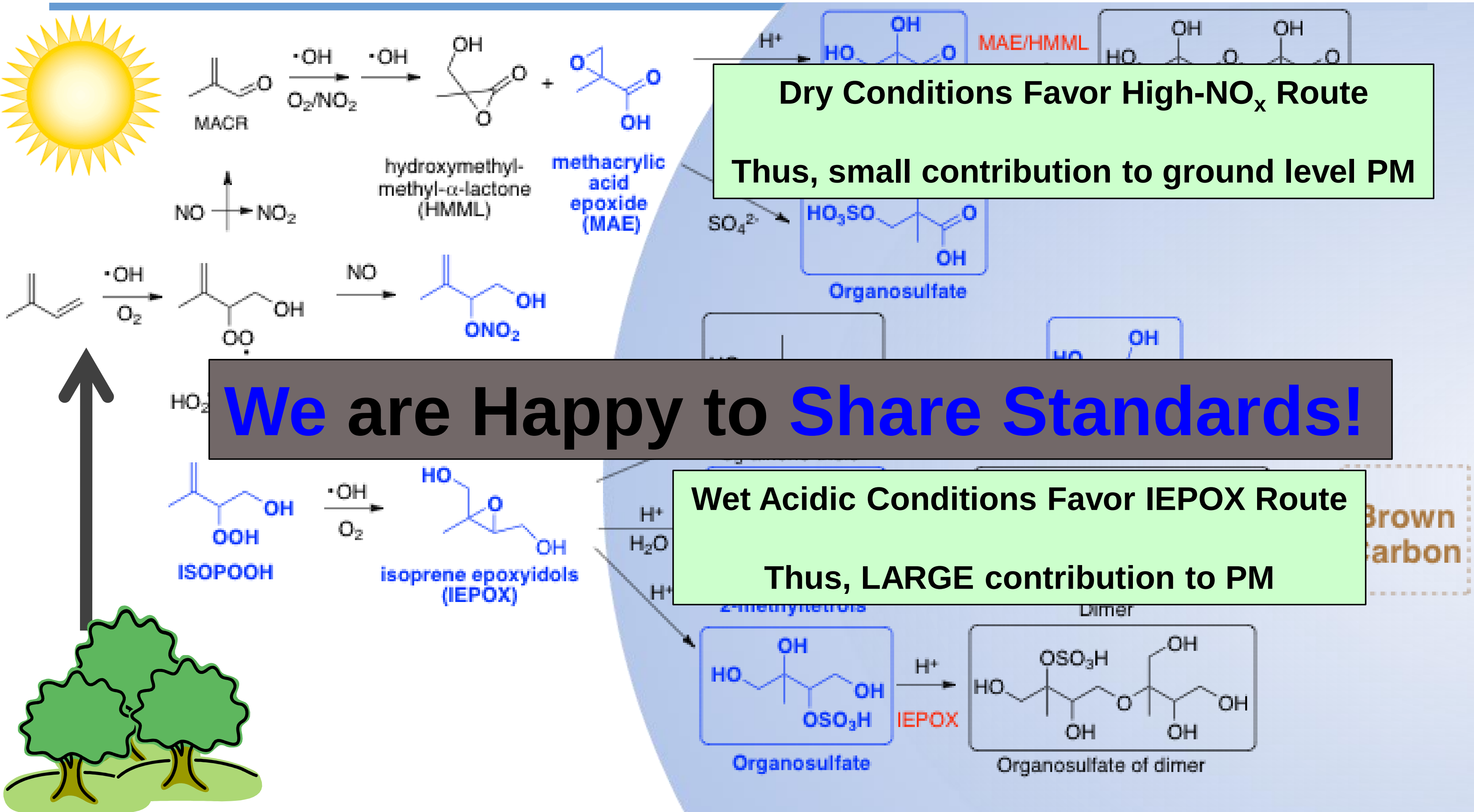


Dry Conditions Favor High-NO_x Route

Thus, small contribution to ground level PM

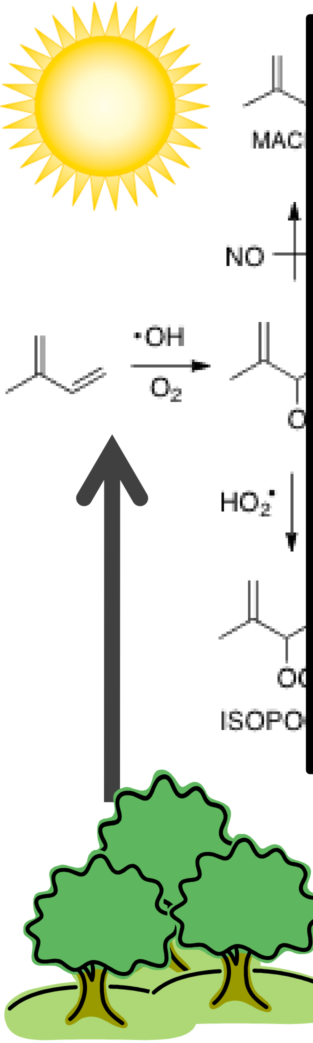
We are Happy to Share Standards!

Wet Acidic Conditions Favor IEPOX Route

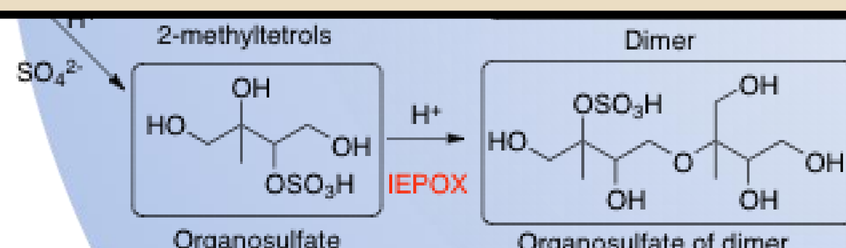
Thus, LARGE contribution to PM

[Lin et al., 2012; Zhang et al. 2012; Lin et al., 2013; Jacobs et al., 2014; Lin et al., 2014; Budisulistiorini et al., 2015; Krechmer et al., 2015; Zhang et al., 2015]

Multiphase Chemistry of Isoprene-Derived Oxidation Products Promote SOA Formation



- Isoprene-derived epoxides are critical to SOA formation from isoprene oxidation
  - What is the actual reactive flux of epoxides to the particle phase?
  - What fraction of uptaken epoxides make SOA?



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

Measuring Reactive Uptake

From linear fit:

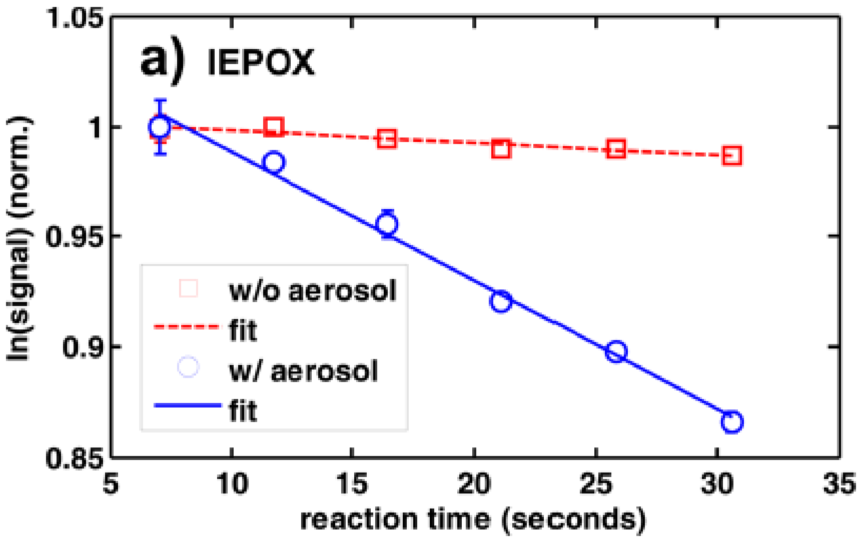
$$k_{total} = -m$$

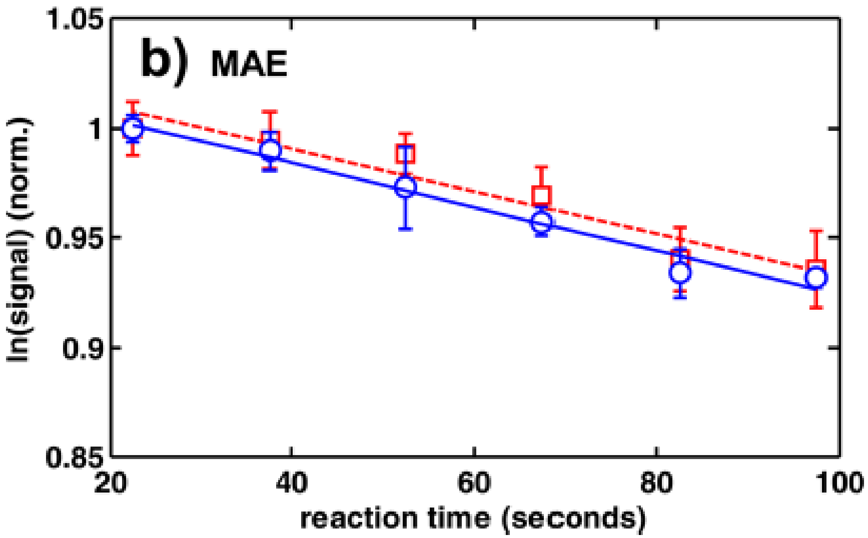
$$k_{wall} = -m$$

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

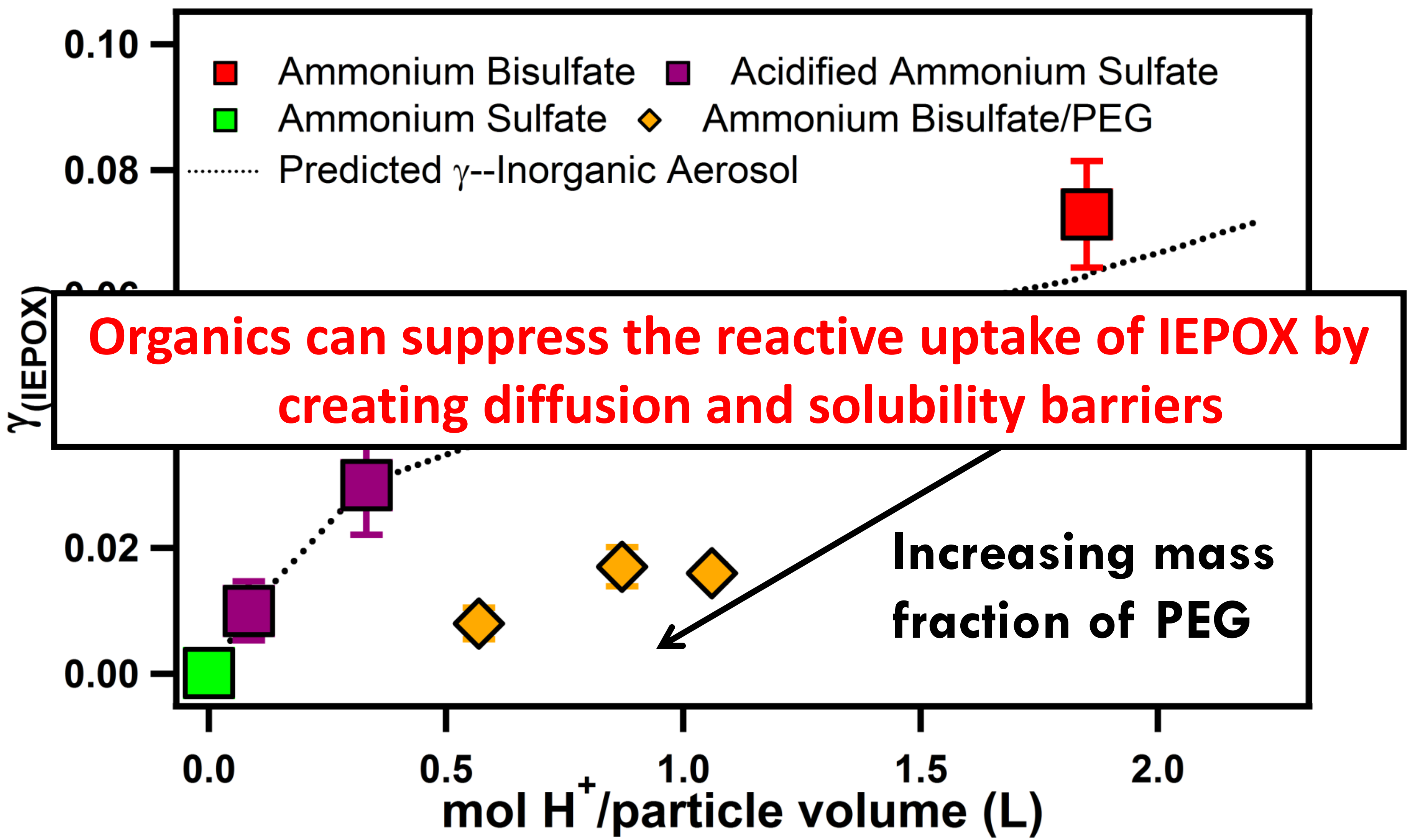
$$\gamma \approx \frac{4k_{het}}{S_a \omega}$$

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



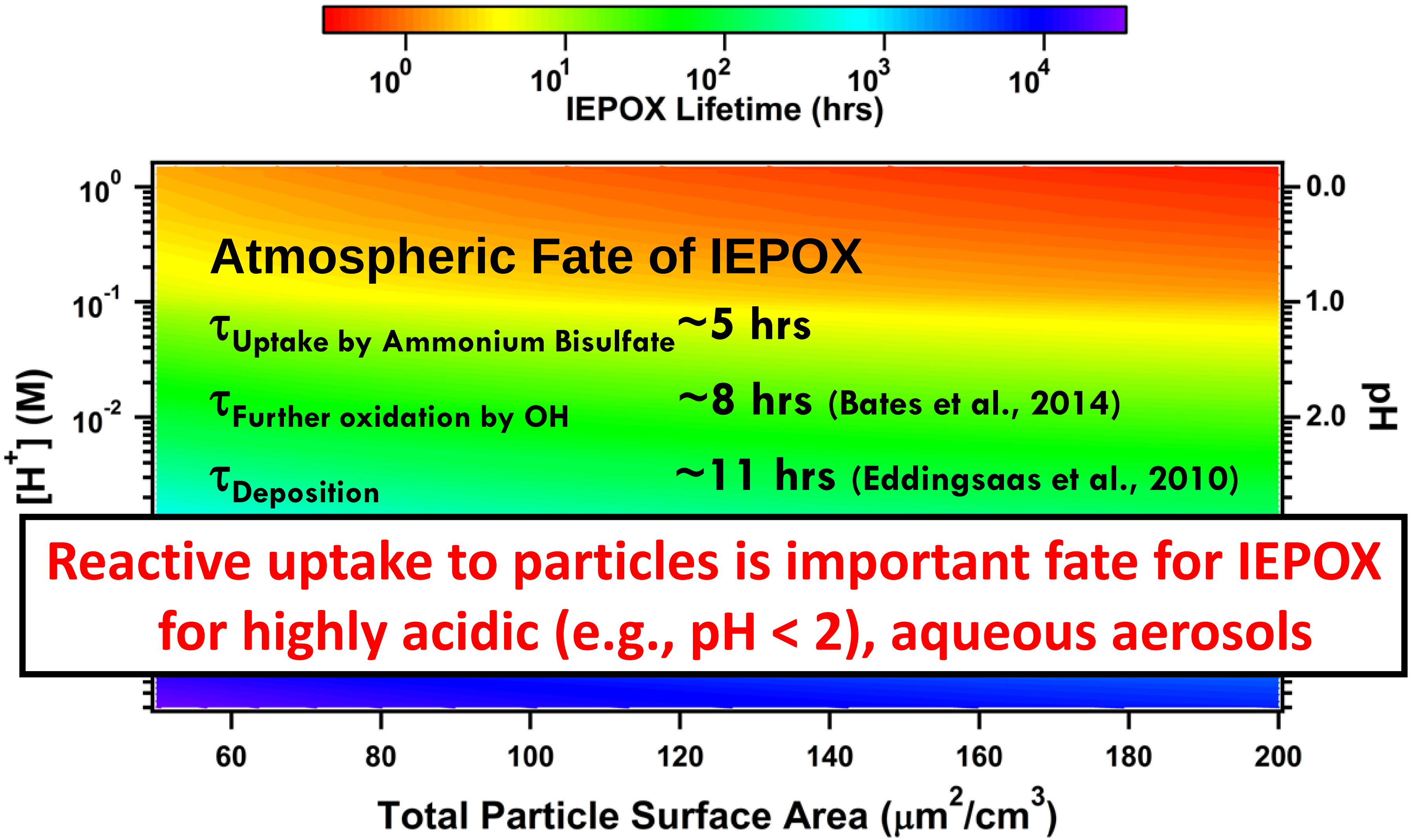


γ Results



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

Reactive Uptake of IEPOX Competitive with Other Loss Processes



Atmospheric Fate of IEPOX

$\tau_{\text{Uptake by Ammonium Bisulfate}}$ ~5 hrs

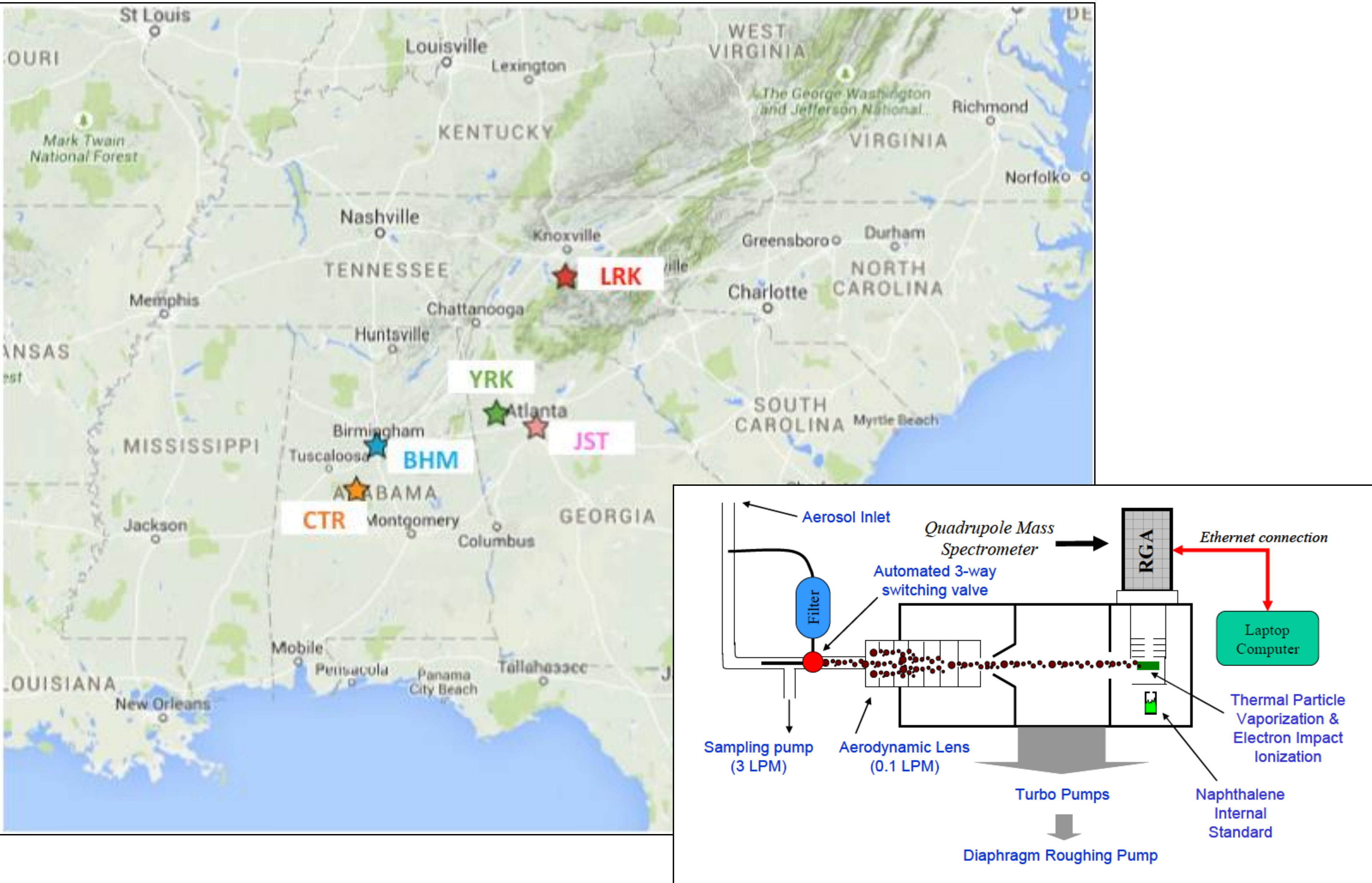
$\tau_{\text{Further oxidation by OH}}$ ~8 hrs (Bates et al., 2014)

$\tau_{\text{Deposition}}$ ~11 hrs (Eddingsaas et al., 2010)

Reactive uptake to particles is important fate for IEPOX for highly acidic (e.g., pH < 2), aqueous aerosols

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

Sampling PM_1 in SE USA Using Aerodyne Aerosol Chemical Speciation Monitor (ACSM)



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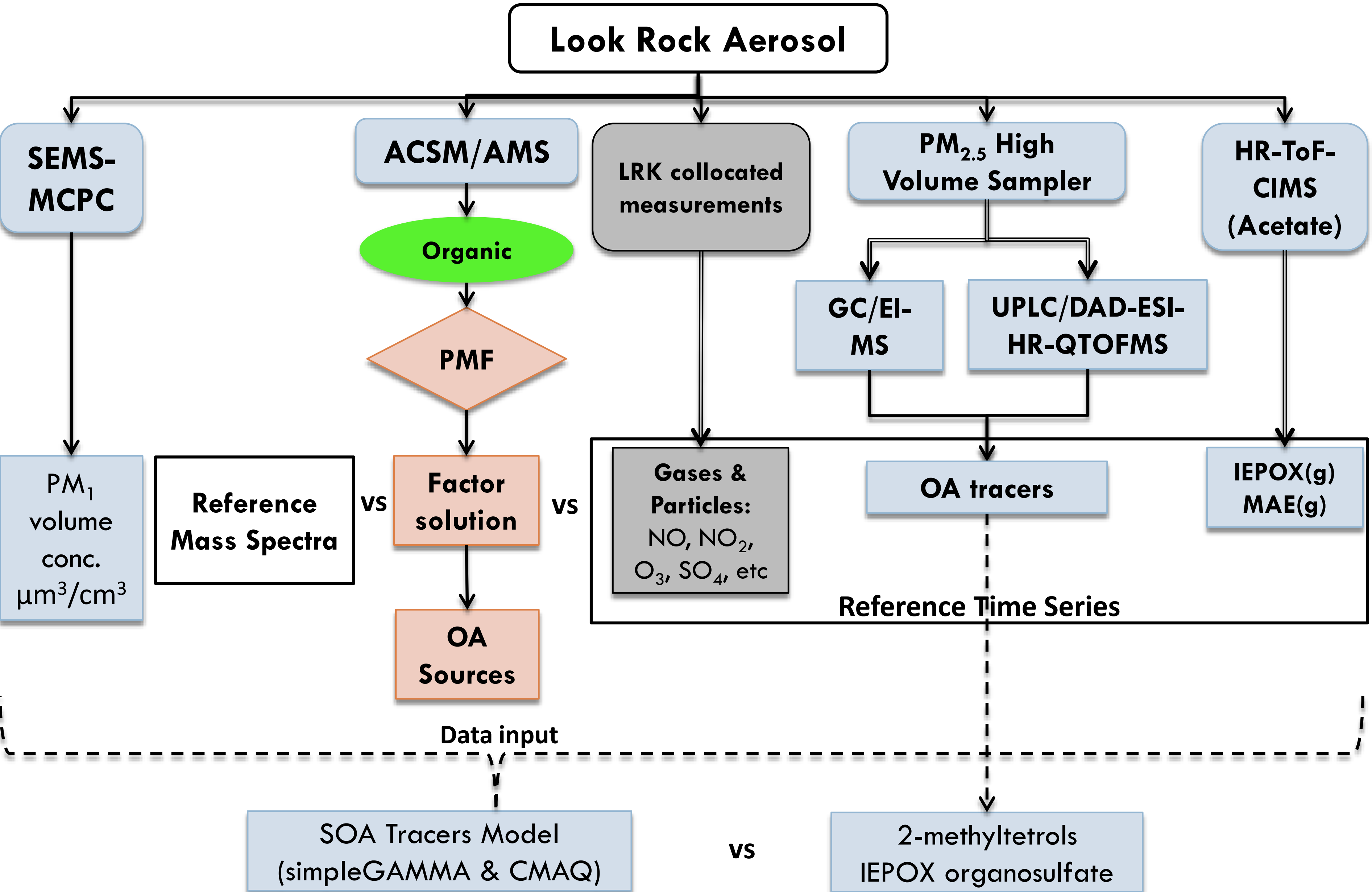
Sampling Approach in SE USA – Look Rock Example



$PM_{2.5}$ Filter Collection & Chemical Analyses for LRK, BHM, CTR & JST Sites – Archive at UNC

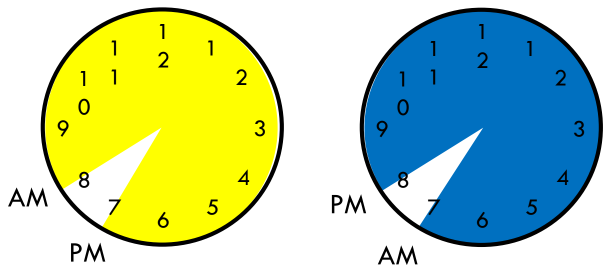
Extracted 2 x 37 mm punches using MeOH → Blow-dried the filtered extract with $N_2(g)$ →

- Derivatized w/ 2:1 BSTFA+TMCS : Pyridine & heated at 70 °C for 1 hr → Analyzed using GC/EI-MS
- Reconstituted w/ 50:50 MeOH : H2O → Analyzed using UPLC/DAD-ESI-Q-TOFMS

Regular 11-hr (59 samples)

Day 08:00 am – 07:00 pm

Night 08:00 pm – 07:00 am (next day)



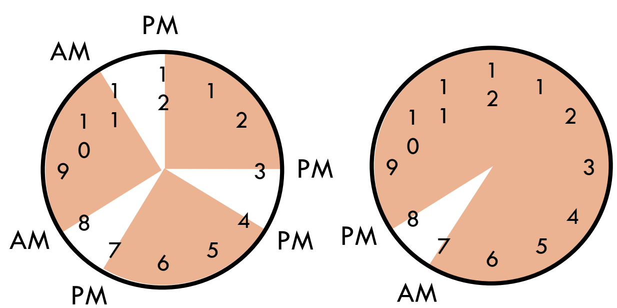
Intensive (64 samples)

08:00 am – 11:00 am

12:00 pm – 03:00 pm

04:00 pm – 07:00 pm

08:00 pm – 07:00 am (next day)



Total number sample: 123 per site

GC/EI-MS tracers

trans-3-MeTHF-3,4-diol

cis-3-MeTHF-3,4-diol

2-methylglyceric acid

2-methylthreitol

2-methylerythritol

(Z)-2-methylbut-3-ene-1,2,4-triol

2-methylbut-3-ene-1,2,3-triol

(E)-2-methylbut-3-ene-1,2,4-triol

UPLC/DAD-ESI-HR-QTOFMS tracers

IEPOX-derived organosulfate

IEPOX-derived dimer organosulfate

MAE-derived organosulfate

$PM_{2.5}$ Filter Collection & Chemical Analyses for LRK, BHM, CTR & JST Sites – Archive at UNC

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SOA tracers	Urban		Rural			
	BHM		CTR		LRK	
	Mean (ng m^{-3})	Average amount detected tracers (%)	Mean (ng m^{-3})	Average amount detected tracers (%)	Mean (ng m^{-3})	Average amount detected tracers (%)
MAE/HMML derived SOA						
MAE/HMML-derived OS	7.2	1.1	10.2	1.3	8.2	1.8
2-methylglyceric acid	10.4	1.7	5.1	0.7	7.5	1.6
IEPOX derived SOA						
IEPOX-derived OS	164.5	24.3	207.1	26.8	139.2	30.3
IEPOX-derived dimer OS	0.04	0.00	0.7	0.1	1.1	0.2
2-methylerythritol	266.7	37.9	204.8	26.5	120.7	26.3
2-methylthreitol	107.3	15.8	73.7	9.5	42.4	9.2
(E)-2-methylbut-3-ene-1,2,4-triol	109.0	12.3	137.3	17.8	98.8	21.5
(Z)-2-methylbut-3-ene-1,2,4-triol	37.3	4.1	50.7	6.6	29.1	6.1
2-methylbut-3-ene-1,2,3-triol	23.4	2.5	26.1	3.4	16.5	3.6
trans-3-MeTHF-3,4-diol	8.6	1.0	0.0	0.0	2.7	0.6
cis-3-MeTHF-3,4-diol	6.8	1.0	0.2	0.0	1.7	0.4

Average loadings of the sum of tracers contributed ~ 7% (up to 20%) & ~ 9% (up to 28%) of total OA mass at BHM and LRK, respectively!

2-methyltetrol/C_5-alkene triol ratio ~ 2.2, nearly double that of CTR and LRK – ozonolysis of isoprene could be one source (Riva et al., 2016, *Atmos. Environ.*)

[Rattanvaraha et al., 2016, *ACPD*]

Real-Time Multi-Year Characterization of NR-PM$_1$ in the S.E. USA using Aerodyne ACSM

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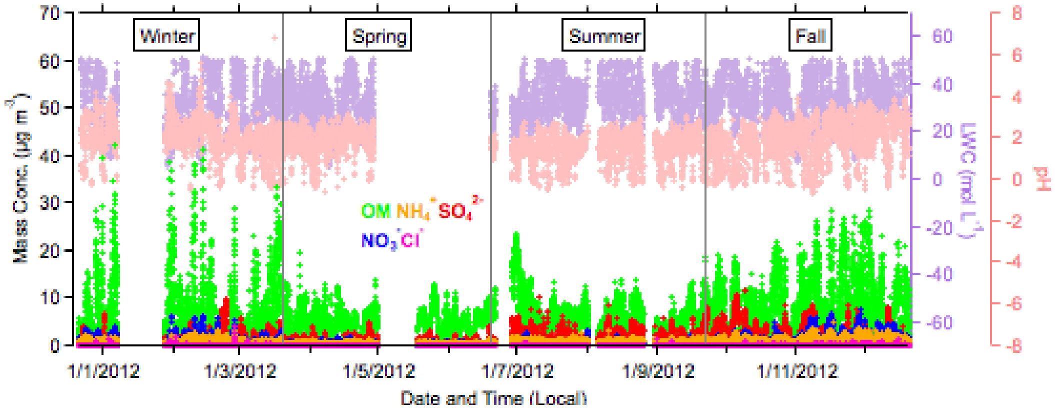
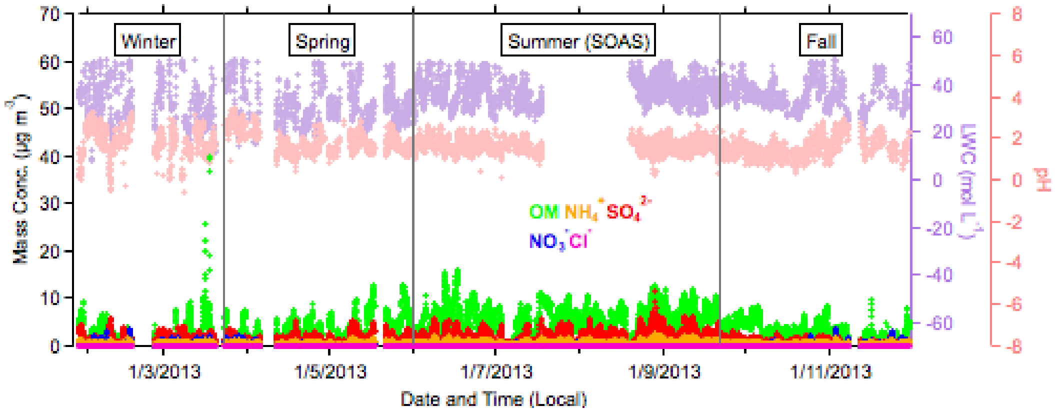
Atlanta, GA 2012

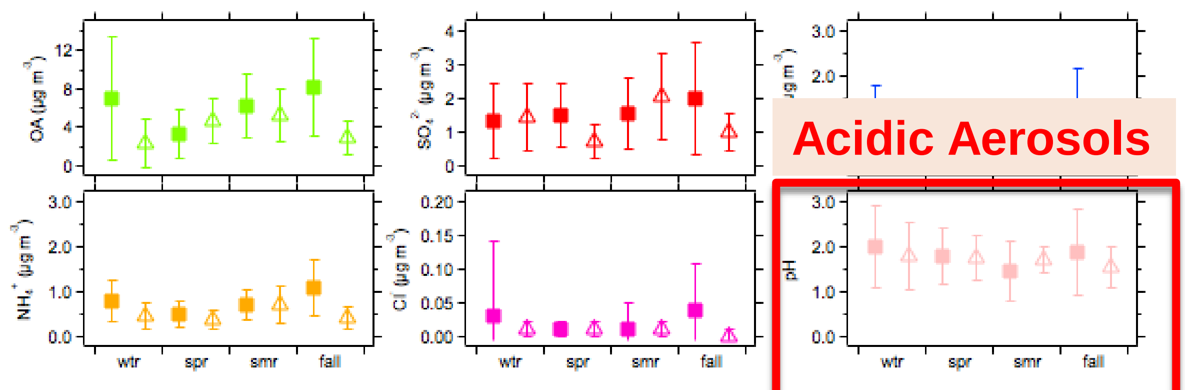


Look Rock, TN 2013



Solid Squares = Atlanta

Open Triangles = Look Rock



[Budisulistiorini et al., 2016, *ACPD*]

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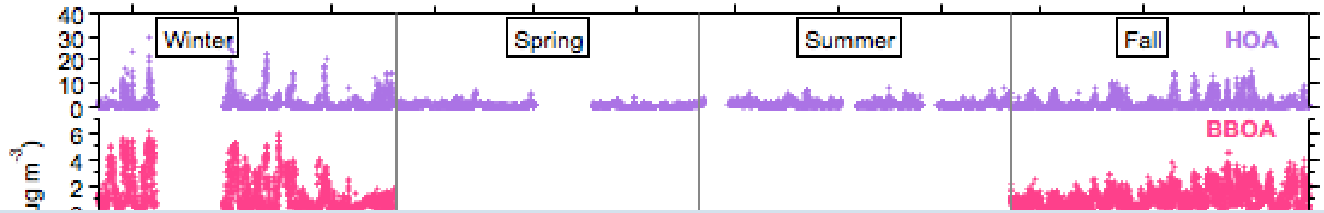
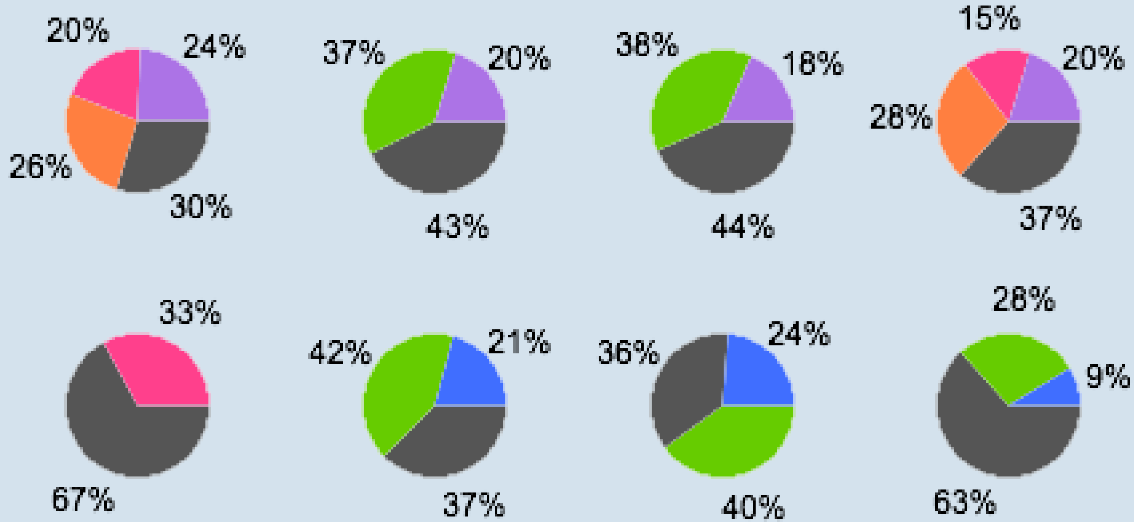
Real-Time Multi-Year Characterization of OA Collected from S.E. USA

Atlanta



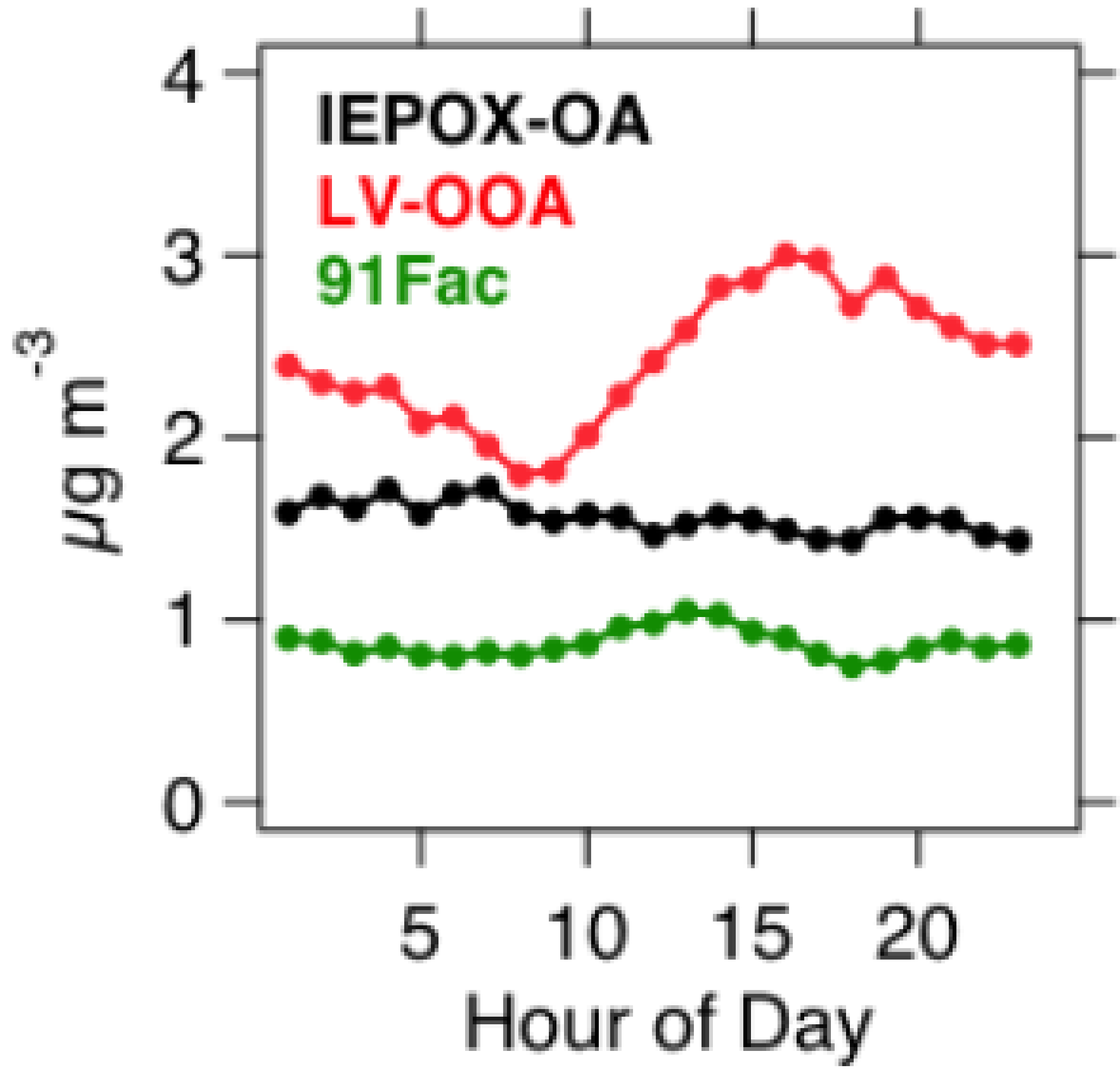


IEPOX-Derived SOA is a MAJOR Fraction of $NR\text{-}PM_1$ in Spring & Summer

Look Rock 2013

[Budisulistiorini et al., 2016, *ACPD*]

Diurnal Variation of Factors at LRK



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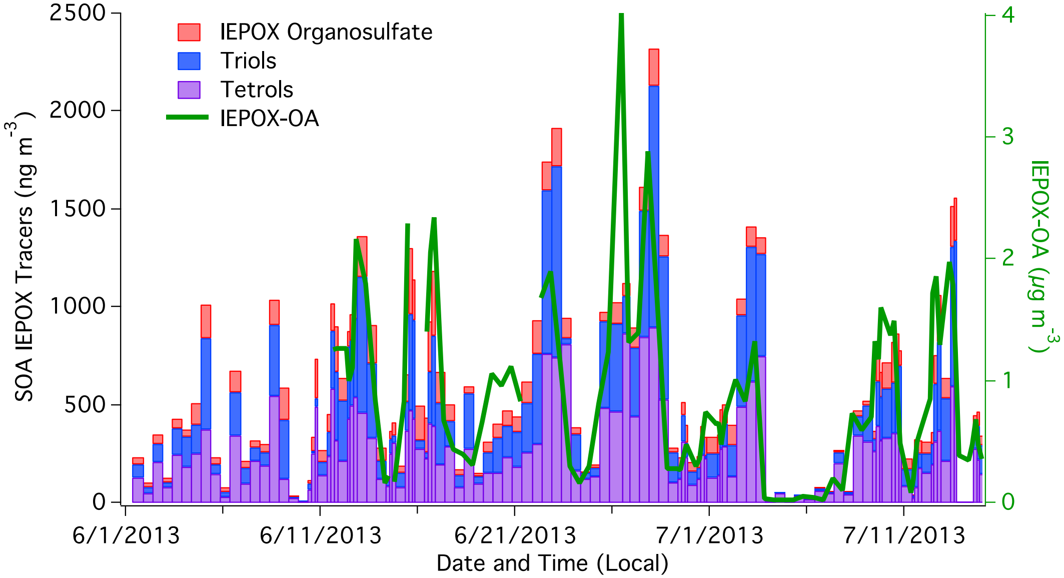
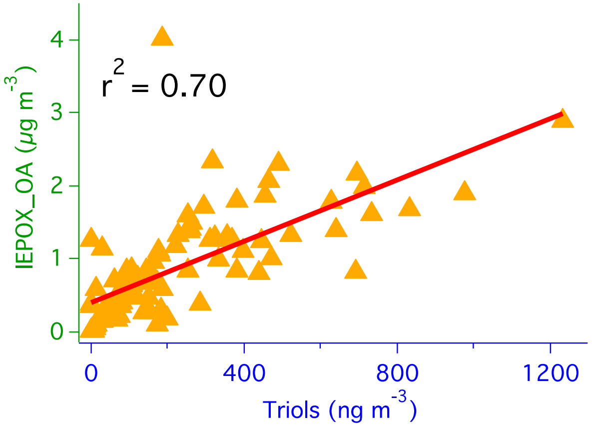
IEPOX-Derived SOA Tracers From Compare Well *VS.* ACSM/AMS IEPOX-OA Factors: Example Centreville (CTR), AL 2013

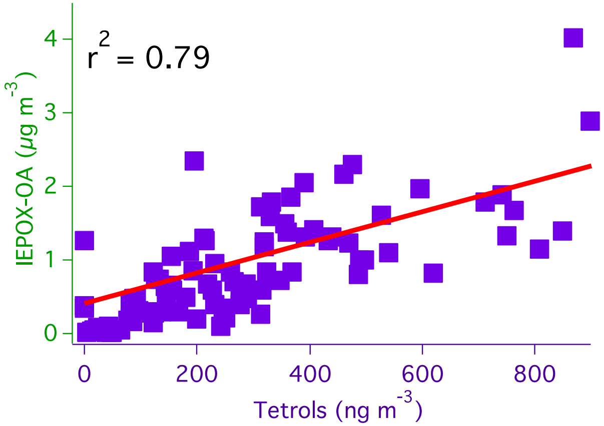


- IEPOX-OA Factor Correlates (R^2 = 0.6) with sulfate loadings at CTR and Look Rock, TN
- IEPOX-OA Factor not correlated with aerosol pH at Centerville, AL [Xu et al., 2015, *PNAS*] or Look Rock, TN [Budisulistiorini et al., 2015, ACP], suggesting some other limiting factor
- IEPOX Tracers Account ~30-50% of IEPOX-OA Factor at LRK. Why? Large Contribution of Oligomers?

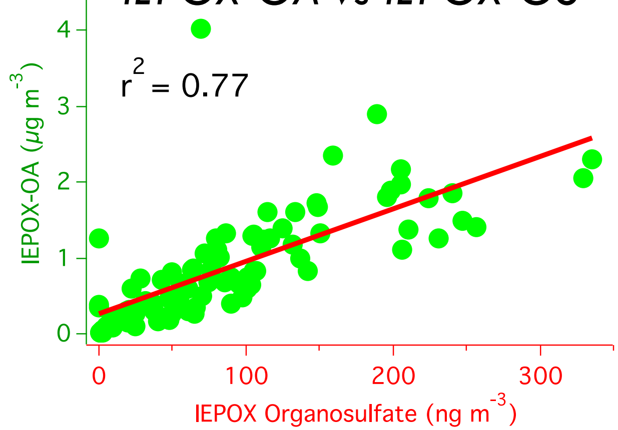
IEPOX-OA vs Triols



IEPOX-OA vs Tetrols



IEPOX-OA vs IEPOX-OS



[Budisulistiorini et al., 2015, ACP; Riva et al., 2016, *in prep*]

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Explicit Isoprene SOA Tracer Modeling of Smog Chamber Data Using Measured Gammas

$$IEPOX_{(g)} \xrightarrow{\gamma} IEPOX_{(aq)}$$

$$k_{het} = \gamma S_a \omega / 4$$

IEPO

IEPO

IEPO

IEPO

IEPO

IEPO

Recent interest in explicit modeling of SOA formation due to model-measurement deviations

- GAMMA: McNeill et al., *ES&T* 2012
- CMAQ: Pye et al., *ES&T* 2013; Karambelas et al., *ES&TL* 2014
- GEOS-Chem: Marais et al., *ACPD* 2015

Need for more constraints on SOA formation kinetics

- experiments and modeling

Gaston et al., *ES&T* 2014; Riedel et al., *ES&TL* 2015

Eddingsaas et al., *JPCA* 2010; Cole-Filipiak et al., *ES&T* 2010; Piletic et al., *PCCP* 2013

IEPOX Chamber SOA Experiments

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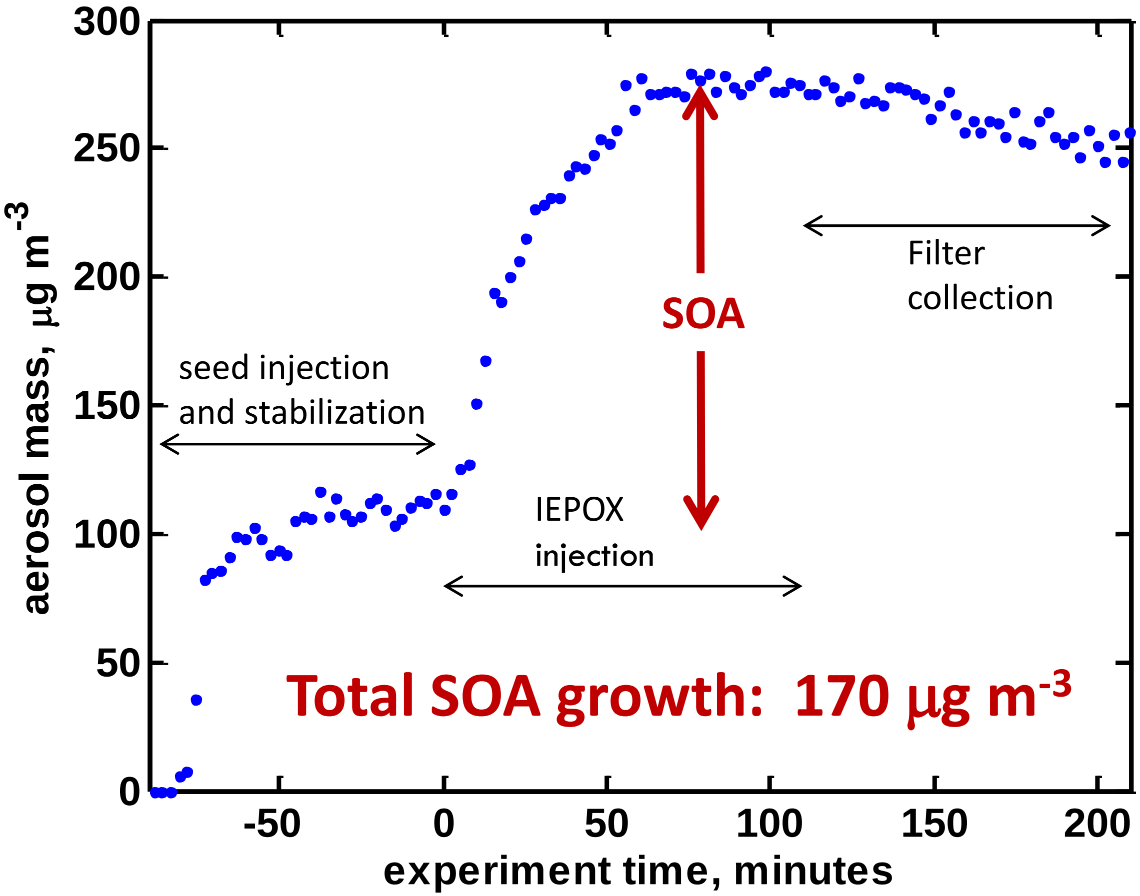
10 m^3 teflon chamber
RH: < 5%
aerosol seed: $(NH_4)_2SO_4 + H_2SO_4$
IEPOX injected: 600 ppbv

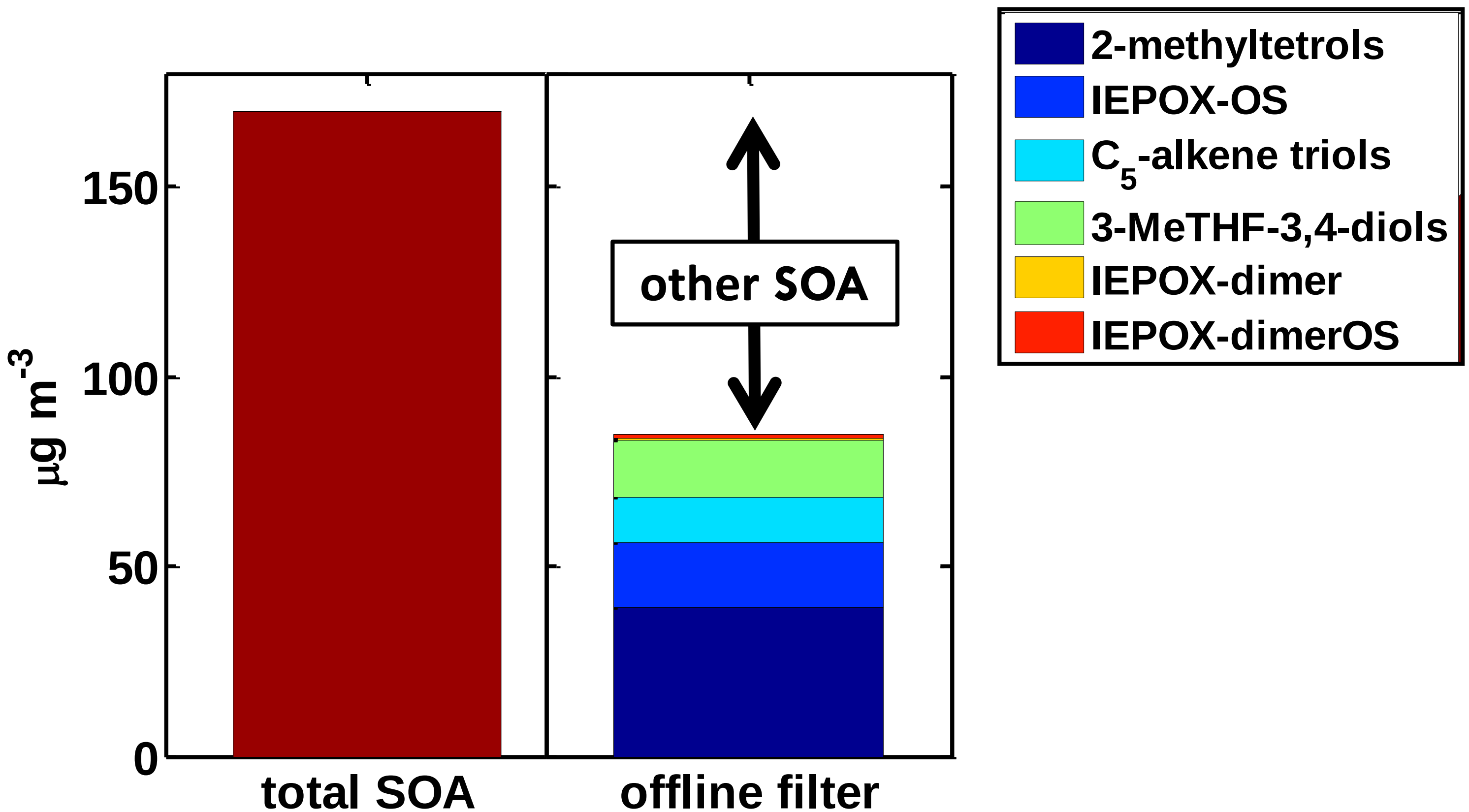


[Riedel et al., 2016, *ACP*]

IEPOX-Derived SOA Tracer Quantification

GC/MS: 2-methyltetrols, C_5-alkene triols, 3-MeTHF-3,4-diols, IEPOX-dimer

LC/ESI-MS : IEPOX-OS, IEPOX-dimerOS



"other SOA" ≡ IEPOX-SOA products not quantified through offline measurements

[Riedel et al., 2016, *ACP*]

Explicit Chamber Model of IEPOX SOA Formation

0-D time-dependent box model

Model run time = experiment duration

Initialize model with:

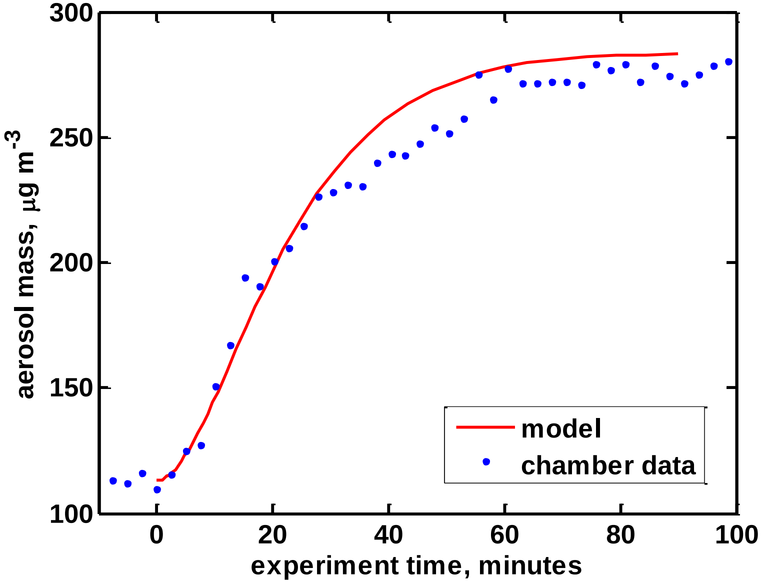
- chamber measured seed aerosol [S_a] and [mass]
- E-AIM calculated seed aerosol composition
  - [SO_4^{2-}], [HSO_4^-], [H_2O], [H^+]
- first-order wall-loss rates applied to $IEPOX_{(g)}$ and seed aerosol
- rate of $IEPOX_{(g)}$ injection simulated by exponential decay
- apply γ = 0.021 derived from Gaston et al. (2014) & Riedel et al. (2015)

Explicitly track:

- $IEPOX_{(g)}$, $IEPOX_{(aq)}$
- 2-methyltetrols, organosulfate, C_5-alkene triols, 3-MeTHF-3,4-diols, IEPOX dimer, IEPOX dimer organosulfate, other SOA
- [SO_4^{2-}], [HSO_4^-]

Vary model aqueous rate constants to minimize difference between model output and filter measurements

Explicit Chamber Model Output



RH: < 5%

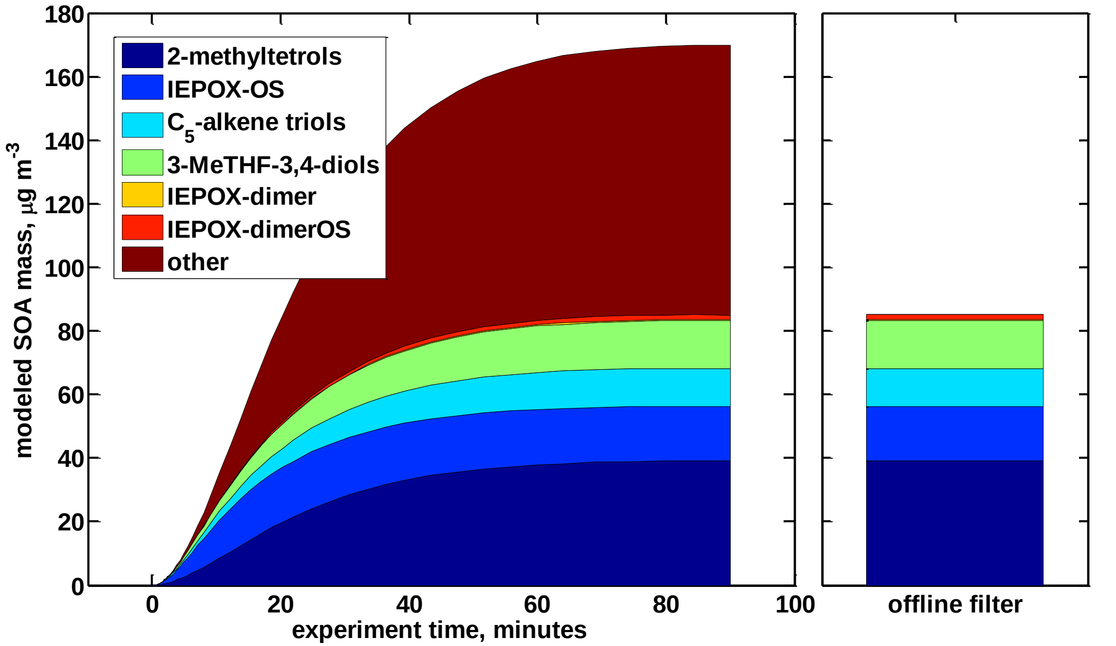
seed: 0.06M $(NH_4)_2SO_4$ + H_2SO_4

IEPOX injected: 5, 15, 30 mg

assumed seed density = 1.6 g/mL

assumed SOA density = 1.25 g/mL (Kroll et al., ES&T 2006)

"other SOA" = $DMAtotal_{mass}$ – $sum(filtertracers_{mass})$



[Riedel et al., 2016, *ACP*]

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Model-Estimated Rate Constants

SOA tracer formed	k
2-methyltetrols	$3.4 \pm 3.2 \times 10^{-4}\ M^{-2}\ s^{-1}$
IEPOX-OS	$4.8 \pm 3.4 \times 10^{-4}\ M^{-2}\ s^{-1}$
C_5-alkene triols	$8.8 \pm 3.8 \times 10^{-4}\ M^{-1}\ s^{-1}$
3-MeTHF-3,4-diols	$2.6 \pm 3.5 \times 10^{-4}\ M^{-1}\ s^{-1}$
IEPOX-dimer	$1.3 \pm 0.7 \times 10^{-5}\ M^{-2}\ s^{-1}$
IEPOX-dimerOS	$6.8 \pm 4.6 \times 10^{-5}\ M^{-2}\ s^{-1}$
other SOA	$5.7 \pm 6.9 \times 10^{-4}\ M^{-2}\ s^{-1}$

Riedel et al., (2016, ACP)

Consistent with Eddingsaas et al. (2010, JPCA) & Cole-Filipiak et al. (2010, ES&T)

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

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

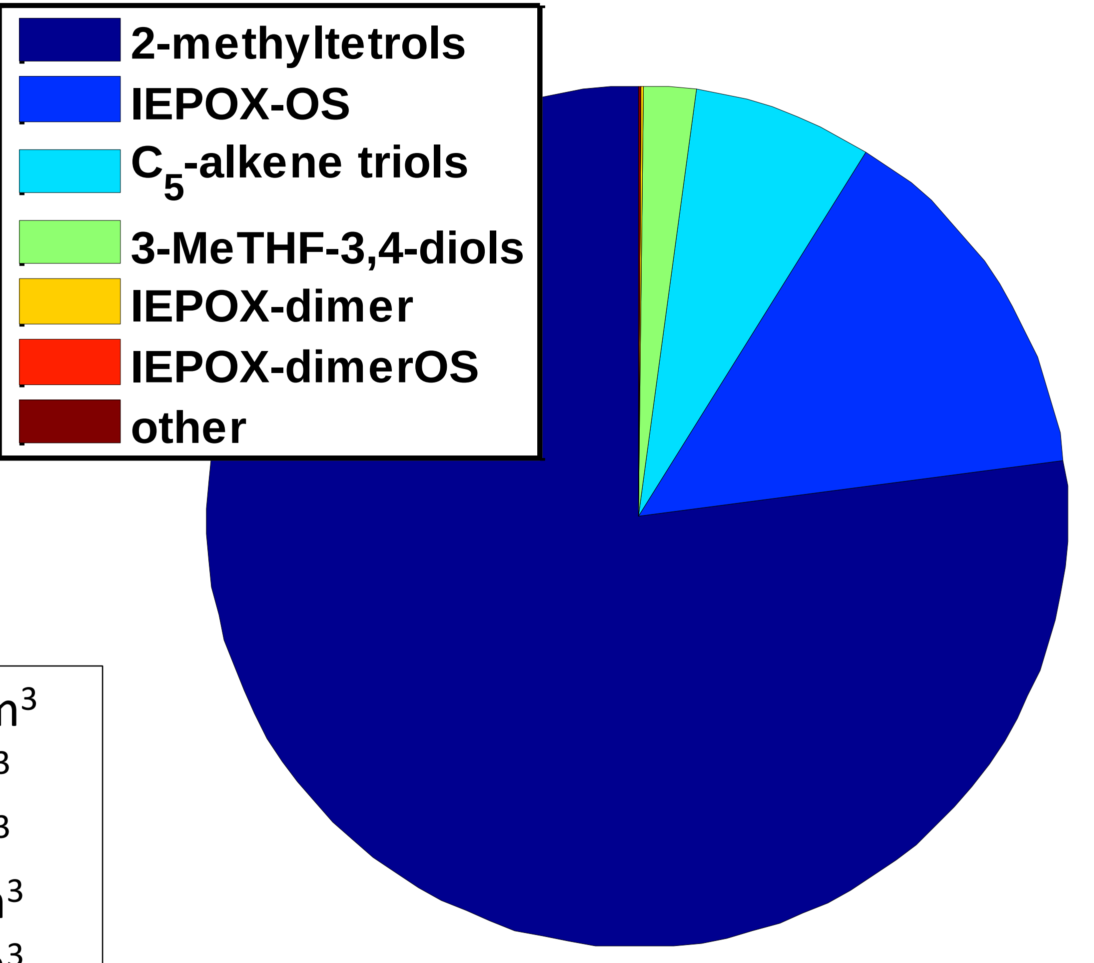
$k \approx 9e\text{-}4\ M^{-2}\ s^{-1}$

$k \approx 2e\text{-}4\ M^{-2}\ s^{-1}$

Atmospheric-Type Simulation

Initialize with:

500 pptv IEPOX
ammonium bisulfate aerosol
250 μm^2/cm^3 aerosol S_a
50% RH
6-hour processing time



2-methyltetrols	288 ng/m^3
IEPOX-OS	52 ng/m^3
C_5-alkene triols	25 ng/m^3
3-MeTHF-3,4-diols	7.4 ng/m^3
IEPOX-dimer	0.1 ng/m^3
IEPOX-dimerOS	0.1 ng/m^3
other SOA	0.6 ng/m^3

Total predicted SOA mass = 0.37 μg m^{-3}

[Riedel et al., 2016, *ACP*]

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What's Certain & Remaining Questions

- We can model explicit SOA tracers from chamber studies; could be extended to field observations from SOAS & GoAMAZON – role of organic coatings/mixtures with sulfate? Why acidity not limiting factor?

- IEPOX SOA large fraction (~1/3) of OA mass in both rural & urban areas of S.E. U.S. during summer; MAE/HMML-derived SOA is minor (at least at surface); Non-IEPOX SOA from ISOPOOH + OH could represent up to 20-25% of OA mass in rural areas

- Role of multiphase chemistry of isoprene-derived peroxides in SOA formation likely important & requires more detailed examination

- Isoprene SOA-induced ROS activates the Nrf2 signaling pathway against oxidative stress – health implications (see my computer!)

- **Policy Question:** Are wet acidic sulfate loadings low enough to prevent potential human health effects?

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Thank You!

Questions?