RUTGERS
THE STATE UNIVERSITY
OF NEW JERSEY

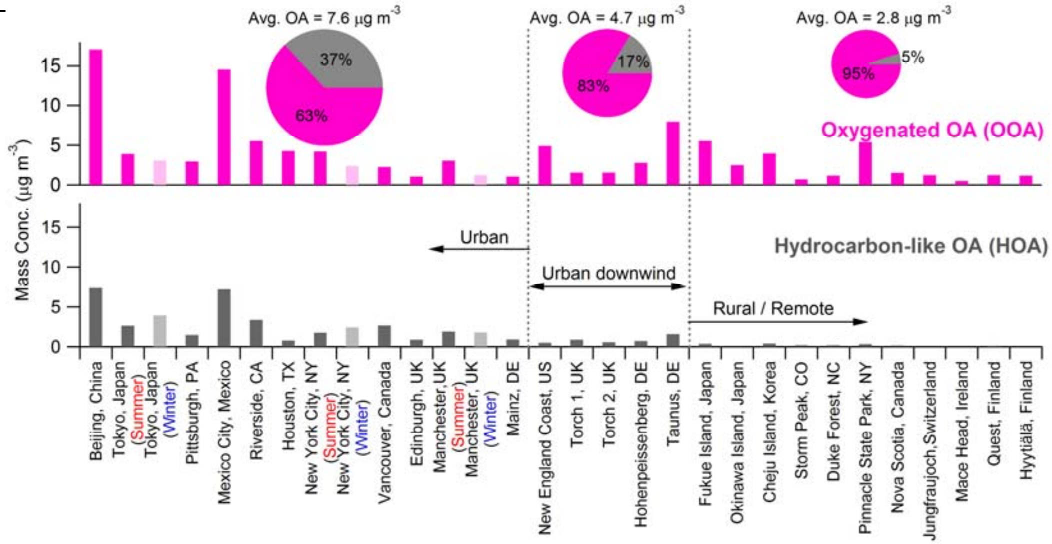
Improved Prediction of In-Cloud Biogenic SOA: Experiments and CMAQ Model Refinements

Barbara Turpin, PI
Sybil Seitzinger, Co-I
Rutgers University
New Brunswick, NJ

SOA – a major fine particle constituent

Aerosol Mass
Spectrometer Data

- 🟩 organic
- 🟥 sulfate
- 🟧 ammonium
- 🟦 nitrate

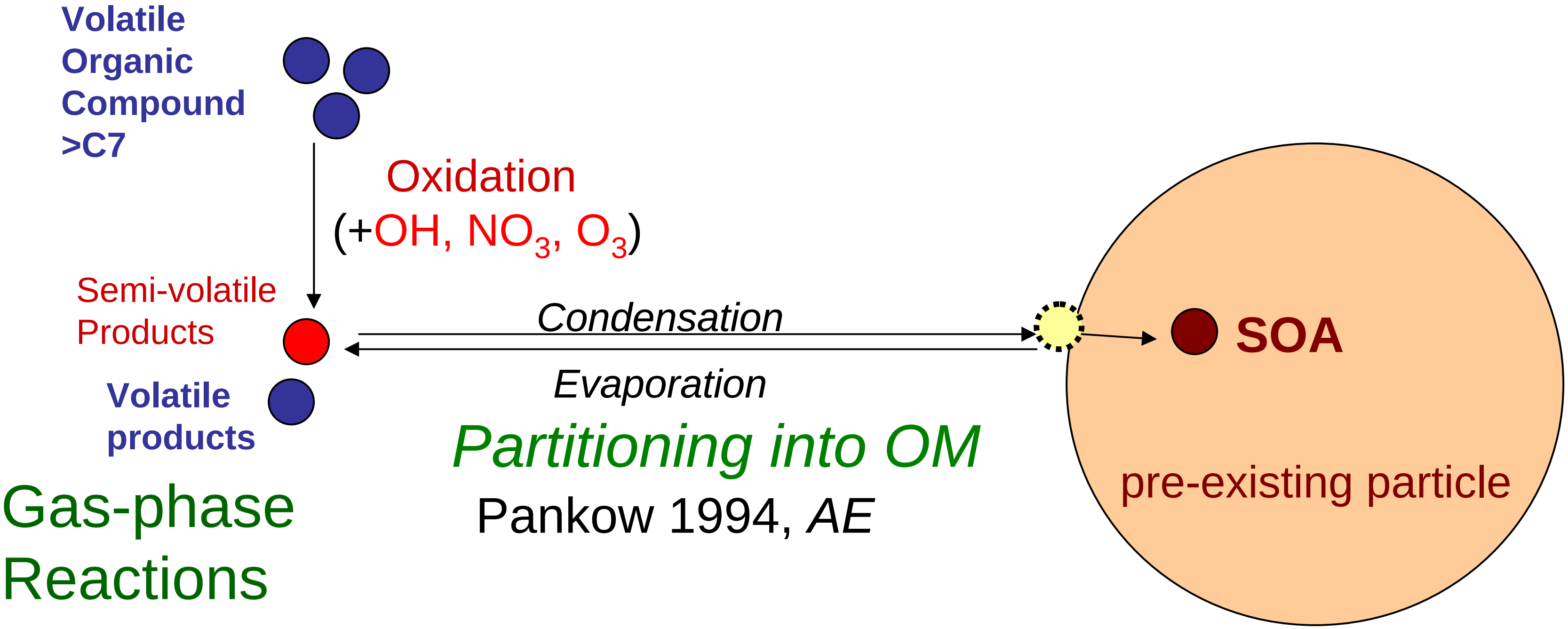


Zhang, Jimenez et al., *GRL*, 34, L13801, 2007

- 🟪 OOA
- ⬛ HOA

Zhang GRL 2007

Traditional “smog chamber” SOA



Volatile Organic Compound >C7

Oxidation (+OH, NO_3, O_3)

Semi-volatile Products

Volatile products

Condensation

Evaporation

SOA

pre-existing particle

Gas-phase Reactions

Partitioning into OM

Pankow 1994, *AE*

Odum 1996, *ES&T*

Precursors must be large (>C7) to produce high yields because partitioning depends on product vapor pressure

While important, fails to explain:

- Predictive models capture organic aerosol poorly (Hallquist ACP 2009)

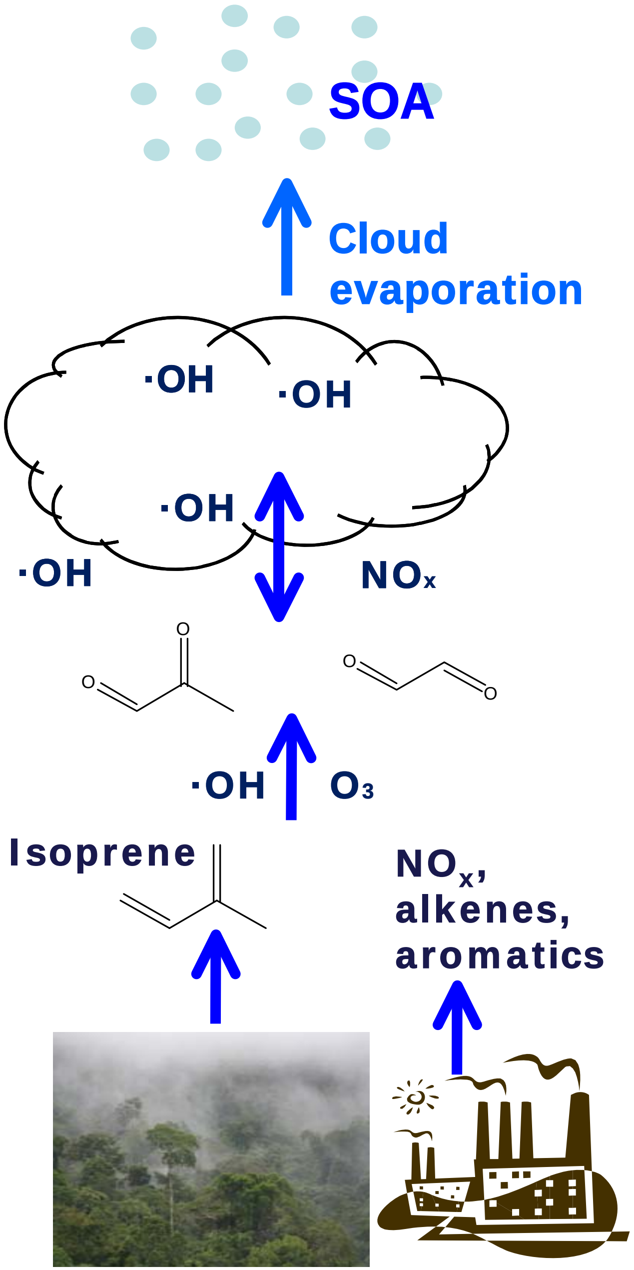
- Atmospheric O/C > smog chamber O/C (Aiken EST 2008)

atmos. HOA = 0.06 – 0.1
atmos. OOA-SV = 0.5 – 0.6
atmos. OOA-LV = 0.8 – 1.0

sm. chamber SOA = 0.3 – 0.5

- Liquid water may be more accessible than OM

  e.g., high humidities of eastern US



In Clouds and Fogs:

Hypothesis: Blando and Turpin, AtmosEnv, 2000
Gelencser and Varga, ACP, 2005

- Organic gases are oxidized forming water-soluble compounds.
- These partition into cloud droplets and react further (e.g., by ·OH).
- Cloud droplets evaporate, lower volatility products remain, forming SOA.

and in Aerosol Water:

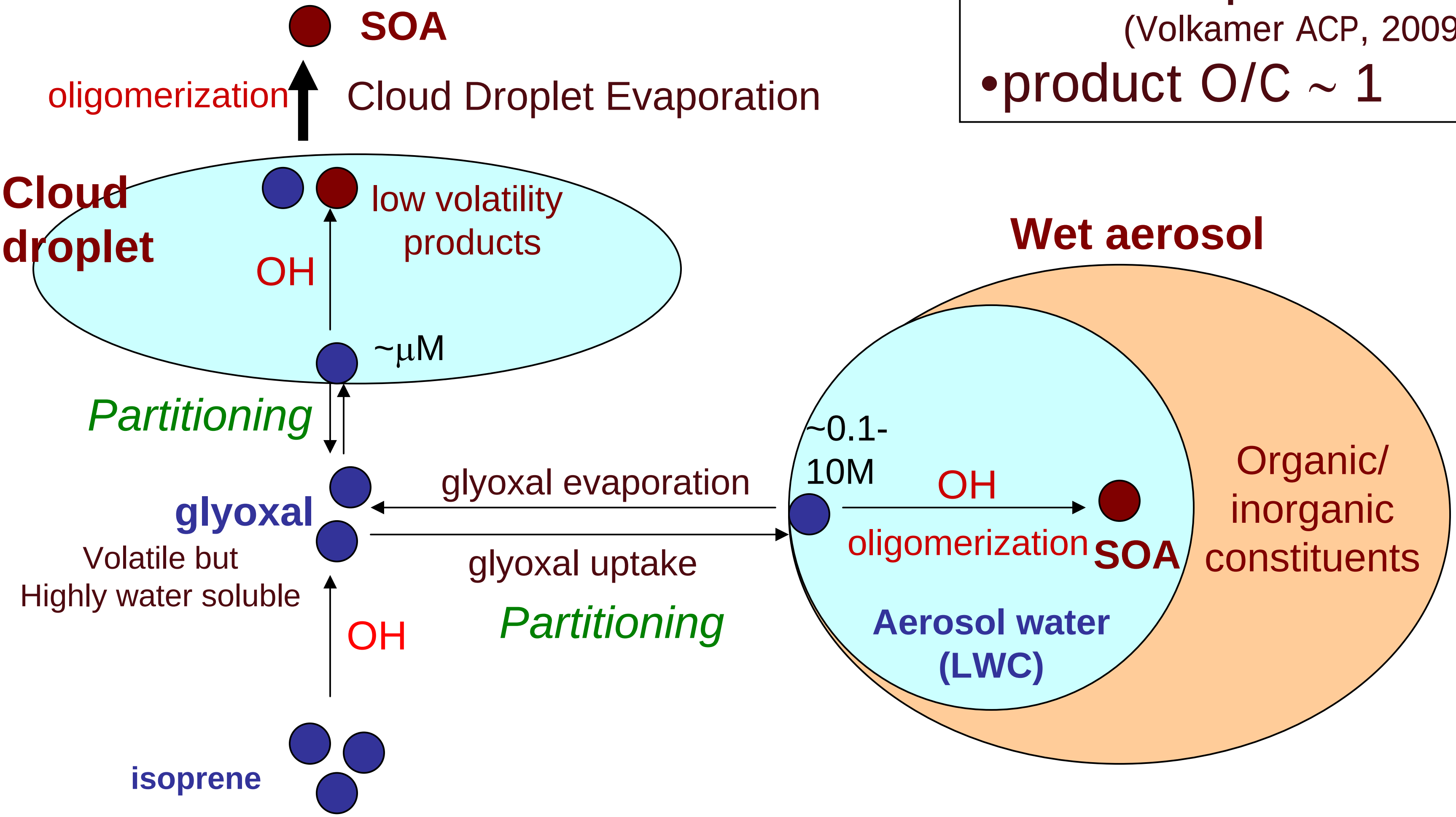
Hypothesis: Carlton AtmosEnv, 2007
Volkamer GRL, 2007

- Water-soluble gases partition into aerosol water and react.
- Lower volatility products remain, forming SOA.

SOA through Aqueous Chemistry:
Partitioning driven by water solubility

Implications

- organic PM loading
- vertical distribution
- different precursors (Volkamer ACP, 2009)
- product O/C ~ 1



SOA

oligomerization

Cloud Droplet Evaporation

Cloud droplet

low volatility products

OH

~µM

Partitioning

glyoxal

Volatile but Highly water soluble

glyoxal evaporation

glyoxal uptake

OH

Partitioning

isoprene

Wet aerosol

~0.1-10M

OH

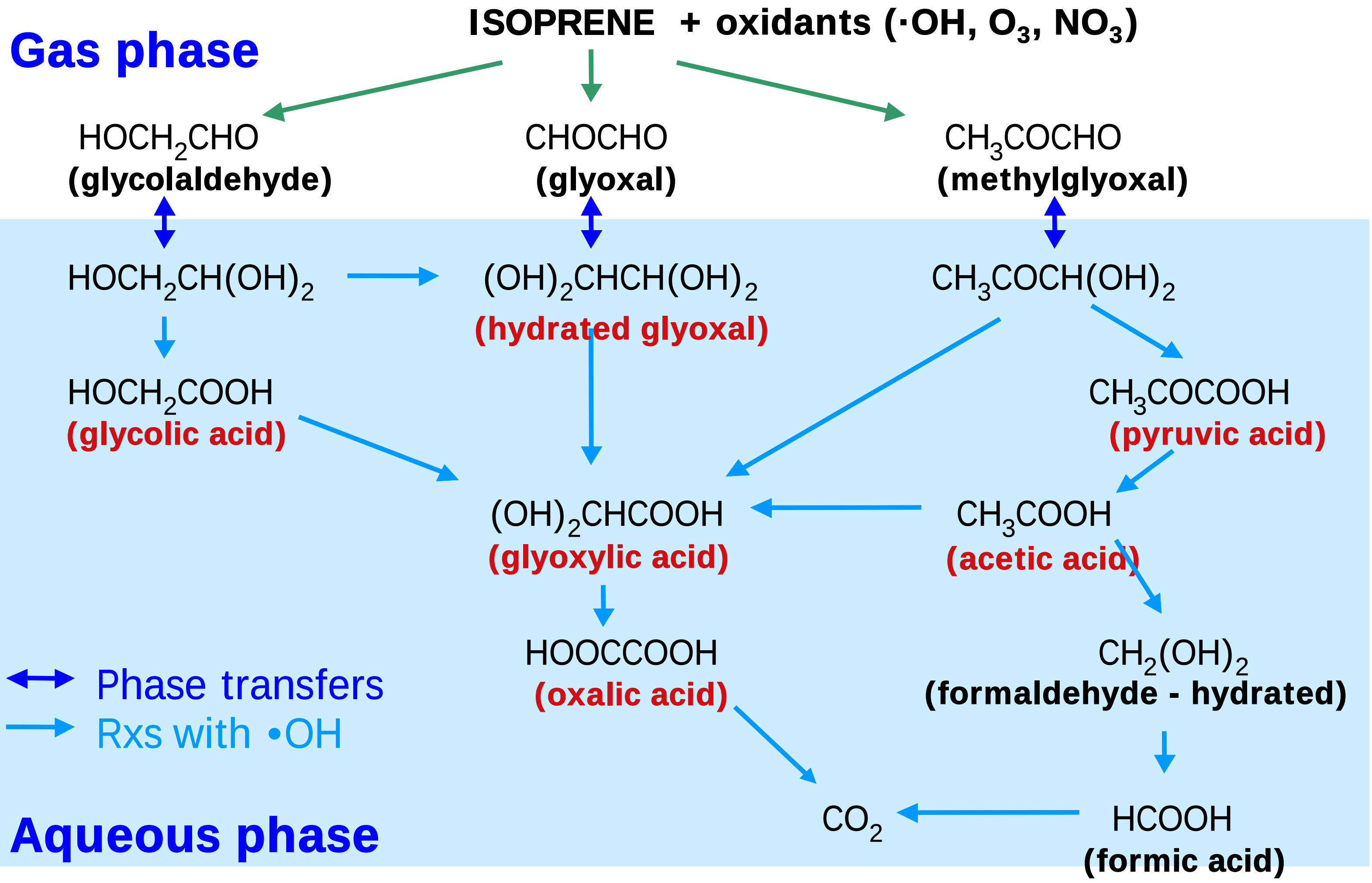
oligomerization

SOA

Organic/ inorganic constituents

Aerosol water (LWC)

Previous research:
Major products of OH radical oxidation verified (≥1mM)



Gas phase

ISOPRENE + oxidants (·OH, O_3, NO_3)

$HOCH_2CHO$
(glycolaldehyde)

$CHOCHO$
(glyoxal)

CH_3COCHO
(methylglyoxal)

$HOCH_2CH(OH)_2$

$(OH)_2CHCH(OH)_2$
(hydrated glyoxal)

$CH_3COCH(OH)_2$

$HOCH_2COOH$
(glycolic acid)

$CH_3COCOOH$
(pyruvic acid)

$(OH)_2CHCOOH$
(glyoxylic acid)

CH_3COOH
(acetic acid)

$HOOCCOOH$
(oxalic acid)

$CH_2(OH)_2$
(formaldehyde - hydrated)

CO_2

$HCOOH$
(formic acid)

↔ Phase transfers
→ Rxs with •OH

Aqueous phase

Carlton *GRL* 2006, *AE* 2007; Altieri *EST* 2006, *AE* 2008; Perri *AE* 2009

Previous research:
Cloud chemistry/parcel model predictions

Demonstrate kinetic feasibility of SOA formation through cloud processing using (mostly) measured rate const.

Rate constants available from cloud and wastewater literature

Herrmann, Monod, Stefan and Bolton

Warneck *AE* 2003; Ervens *JGR* 2004; Lim *EST* 2005

Questions:

How does precursor concentration matter?

How do high molecular weight products form?

Can the chemical model reproduce experiments?

How do anthropogenic emissions impact biogenic “aqueous” SOA formation?

Improved Prediction of In-Cloud Biogenic SOA

Overall Goal:

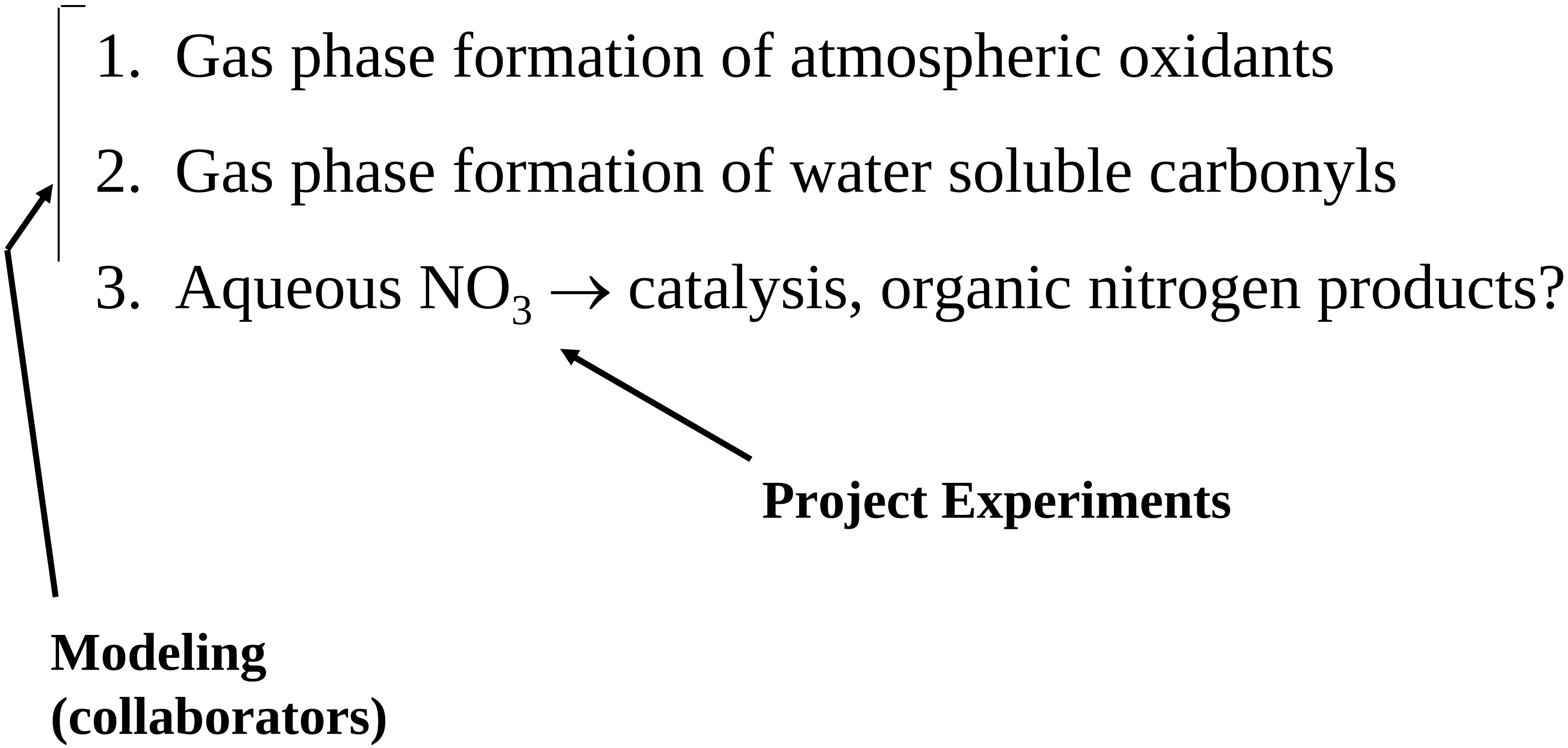
Improve the simulation of secondary organic aerosol (SOA) formation through atmospheric aqueous chemistry

Approach:

- Conduct aqueous experiments at cloud concentrations and ± HNO_3 (glyoxal/ methylglyoxal + OH)
- Validate/refine aqueous chemical mechanisms; update the cloud chemistry model
- Add in-cloud SOA formation to CMAQ
- Begin to explore the magnitude of in-cloud SOA formation and role of NO_x/HNO_3 in SOA formation from isoprene through cloud processing

This Project

Roles of NOx in Aqueous SOA from Isoprene:



1. Gas phase formation of atmospheric oxidants
2. Gas phase formation of water soluble carbonyls
3. Aqueous $NO_3 \rightarrow$ catalysis, organic nitrogen products?

Project Experiments

Modeling
(collaborators)

Aqueous-Phase Reactions with Product Analysis

Goal: Validate/Refine Aqueous Chemistry Model

Experiments

10 - 3000 μM ORG

H_2O_2+hν→ ·OH (~10^{-12} M)

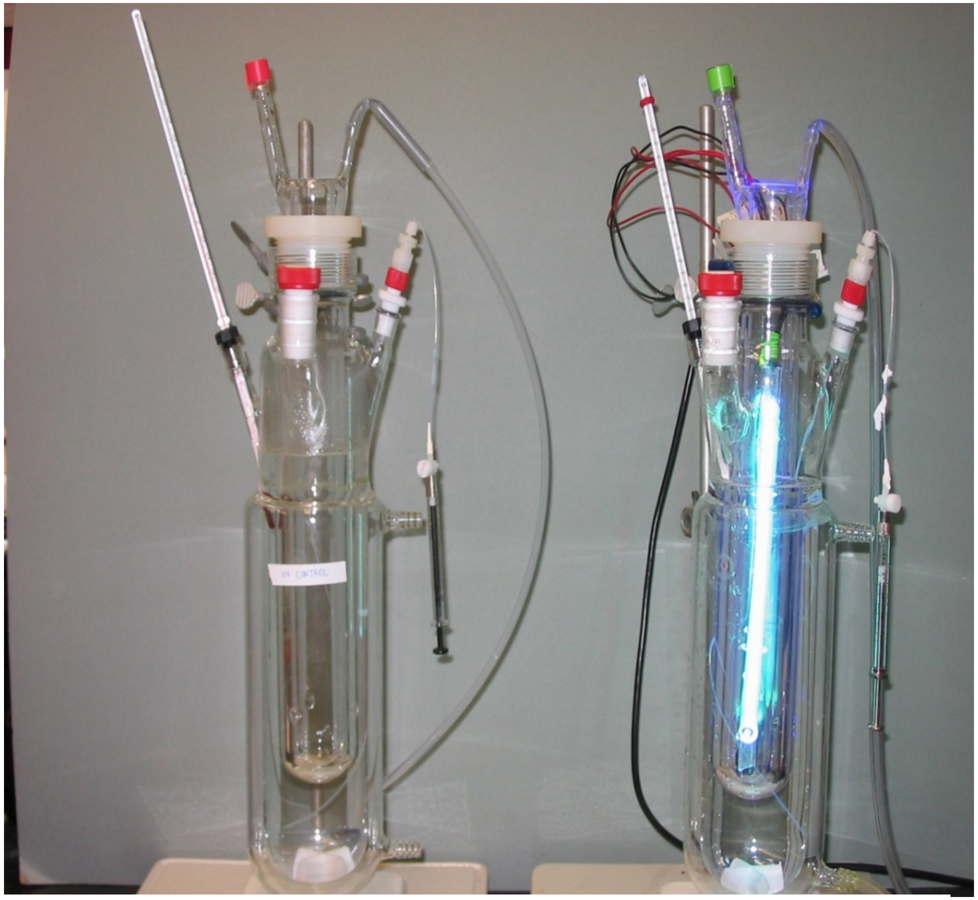
2-5 pH

± HNO_3, NH_4

ORG: glyoxal, methylglyoxal

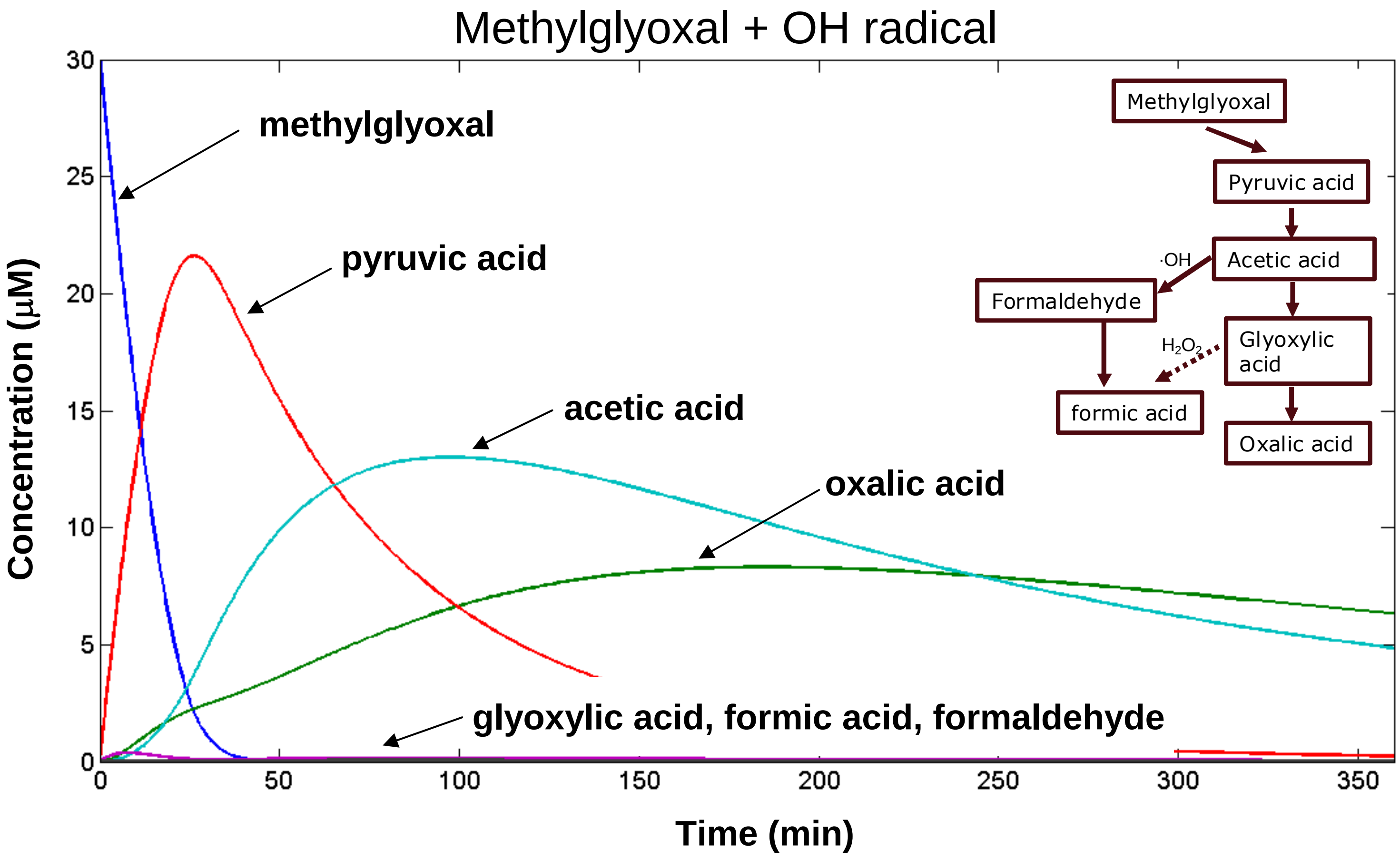
Controls

ORG+Prod+UV ± HNO_3, NH_4
ORG+Prod+H_2O_2 ± HNO_3, NH_4
UV+H_2O_2



On-line ESI MS; IC-ESI-MS; FT-ICR MS; ESI-MS-MS,
UV or IC for organic acids, DOC for mass balance, H_2O_2

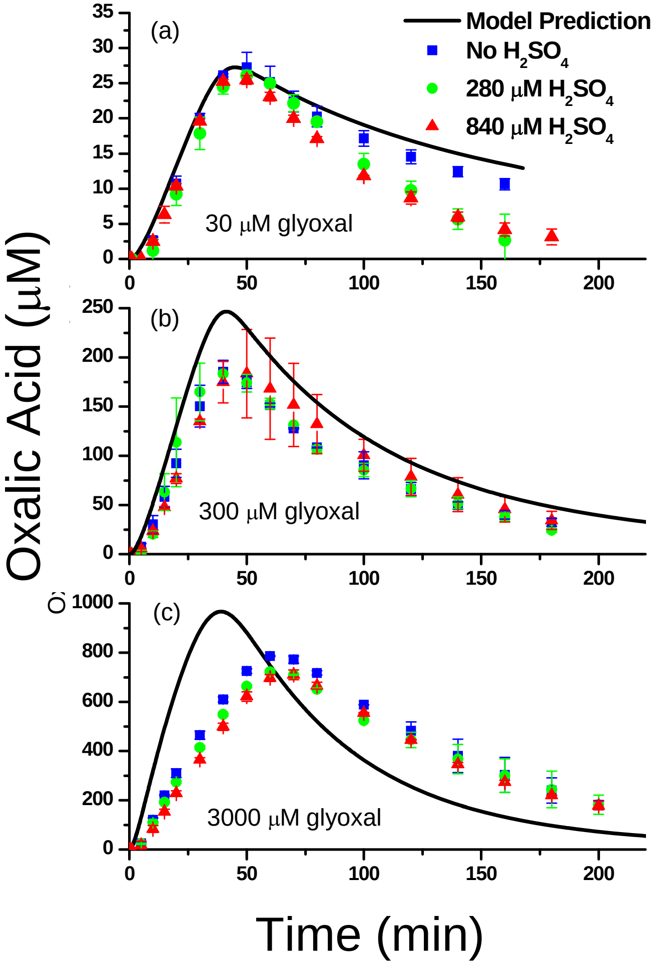
Precursor/products modeled in reaction vessel:



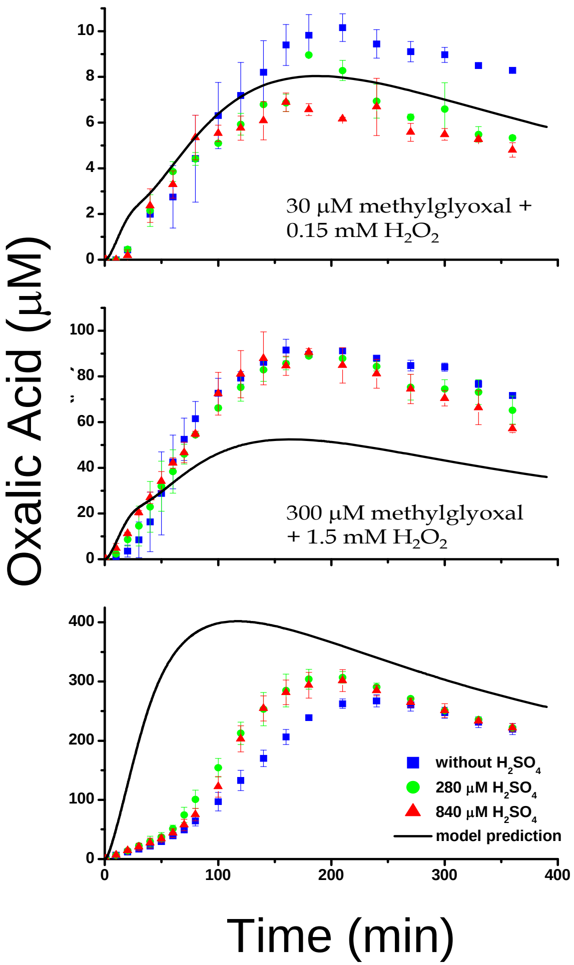
Tan *AE*, 2010

Dilute aqueous chemistry model reproduces oxalic, pyruvic acid and total organic carbon at 30 µM

Glyoxal



Methylglyoxal



Cloud relevant
~30 µM

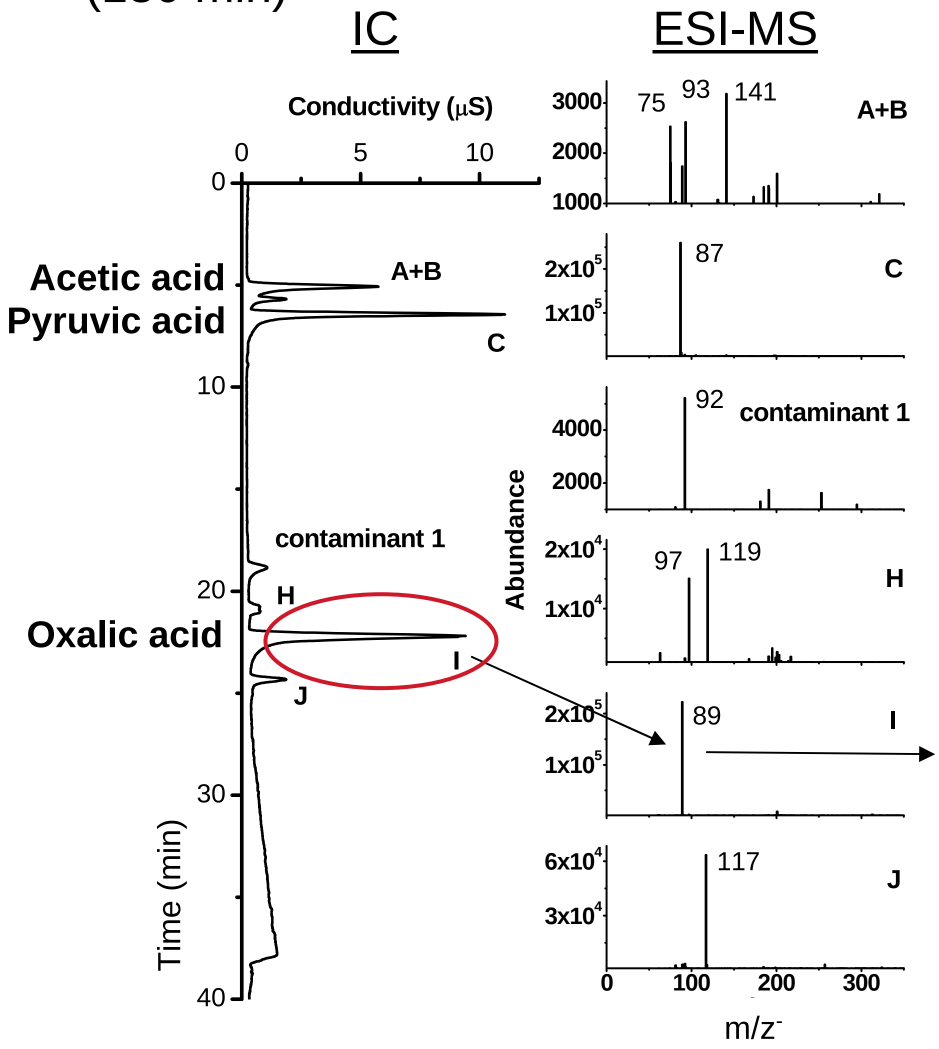
300 µM

3000 µM

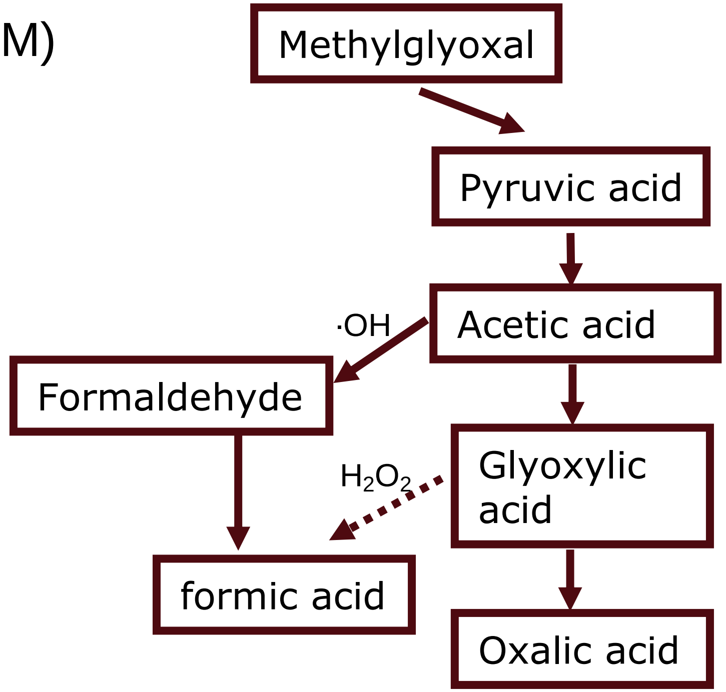
Tan *EST* 2009; *AE* 2010

Oxalate formation verified with IC ESI-MS

Methylglyoxal (3000 μM) + OH radical (10^{-12} M) (180 min)



Oxalic acid (pk I, m/z^- 89)



Methylglyoxal

Pyruvic acid

Acetic acid

·OH

Formaldehyde

Glyoxylic acid

H_2O_2

formic acid

Oxalic acid

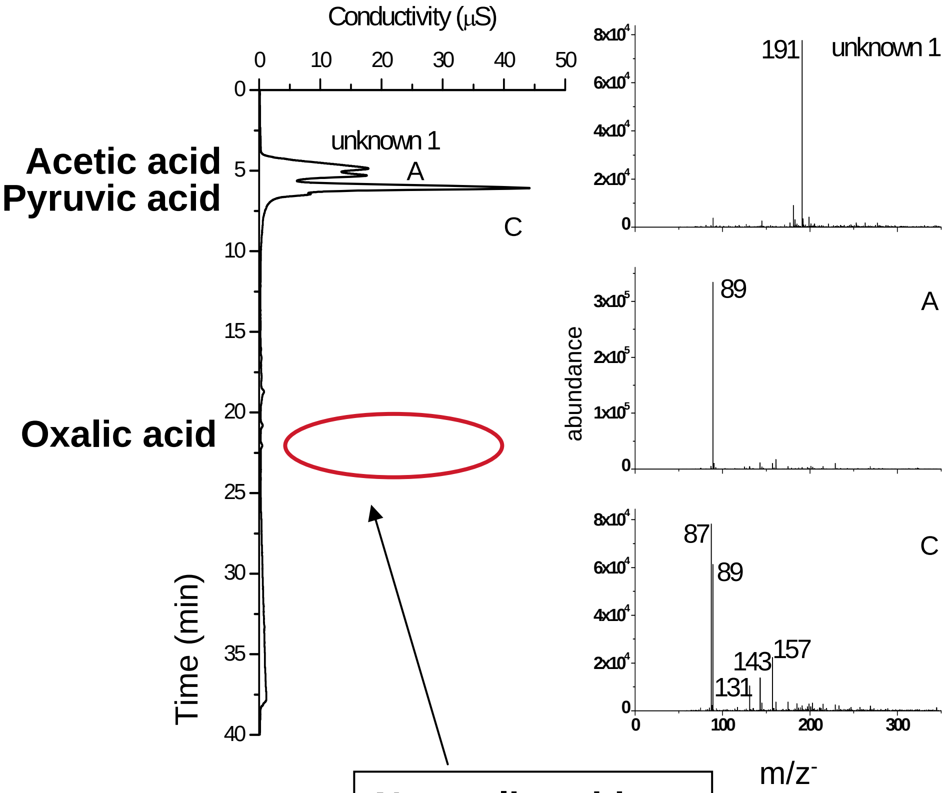
Tan *AE*, 2010

Methylglyoxal experiment with IC ESI-MS

Oxalic acid forms only in the presence of OH radical

Methylglyoxal (3000 μM) + UV (180 min)

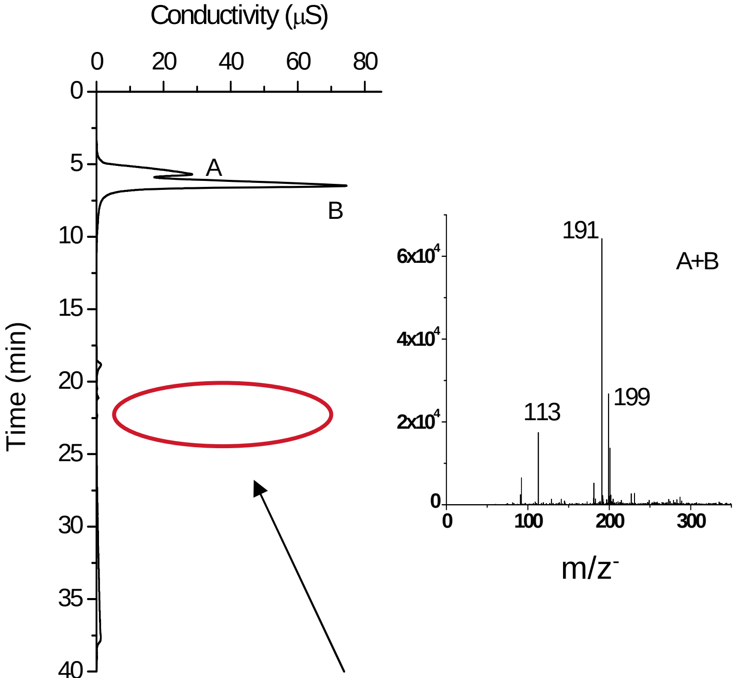
IC ESI-MS



No oxalic acid forms in control experiments

Methylglyoxal (3000 μM) + H_2O_2

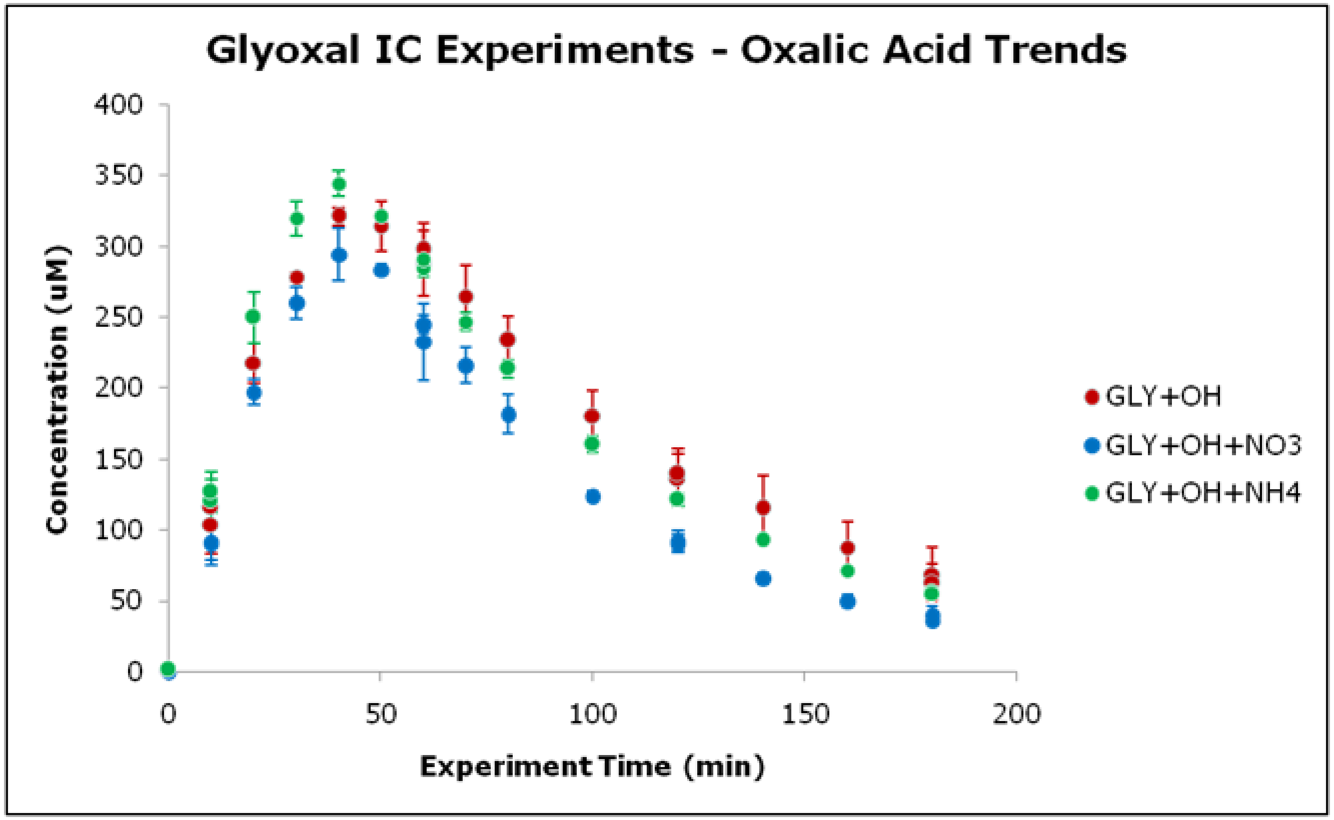
IC ESI-MS



No oxalic acid forms in control experiments

Tan *AE*, 2010

Addition of HNO_3 (1.7 mM) or $(NH_4)_2SO_4$ (0.84 mM) to glyoxal (1 mM) and OH radical (~10^{-12} M)

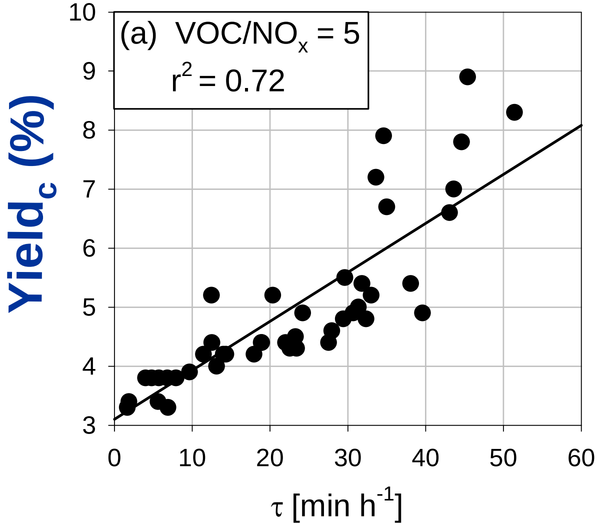


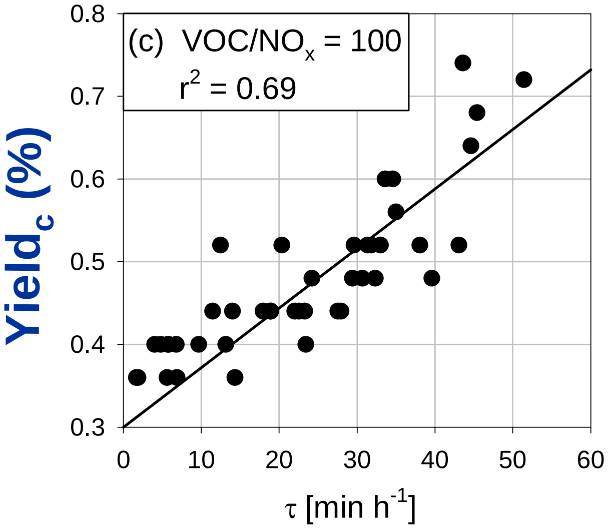
Little effect on oxalate (slighly faster decay with nitric acid)
No change in nitrate or sulfate throughout the reaction
No discernable change in IC ESI-MS
Might still form enough organic-N to observe by FT-ICR MS

Kirkland, in prep

Impact of NOx on SOA from isoprene through cloud proc.

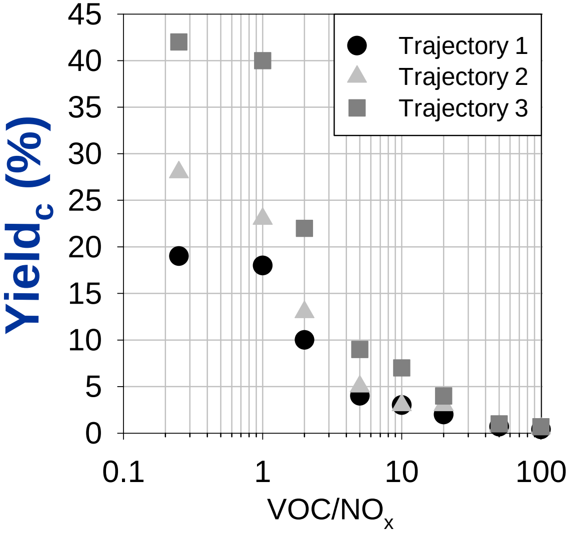
Cloud contact time





Note: higher SOA yields with higher NOx because more gas phase production of water soluble carbonyls

VOC/NOx



Yield (%) =
mass C in SOA
mass isoprene C

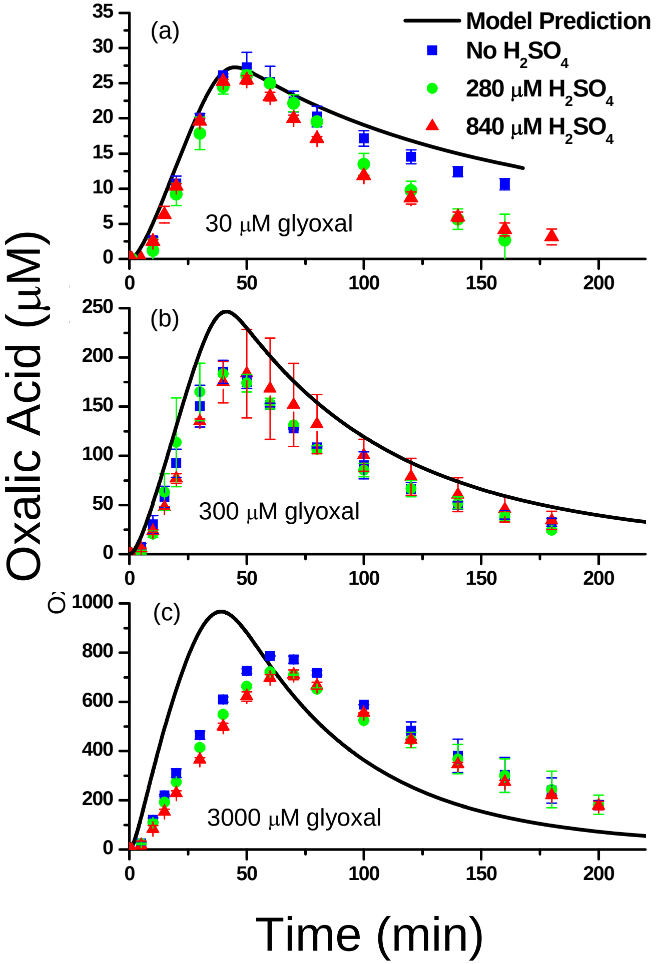
Feingold microphys. cloud model

- multiple cycles
- stratocumulus
- partitioning of wsoc
- gas+aq chem
- Ervens aq chem
- altered Gly, PA chem

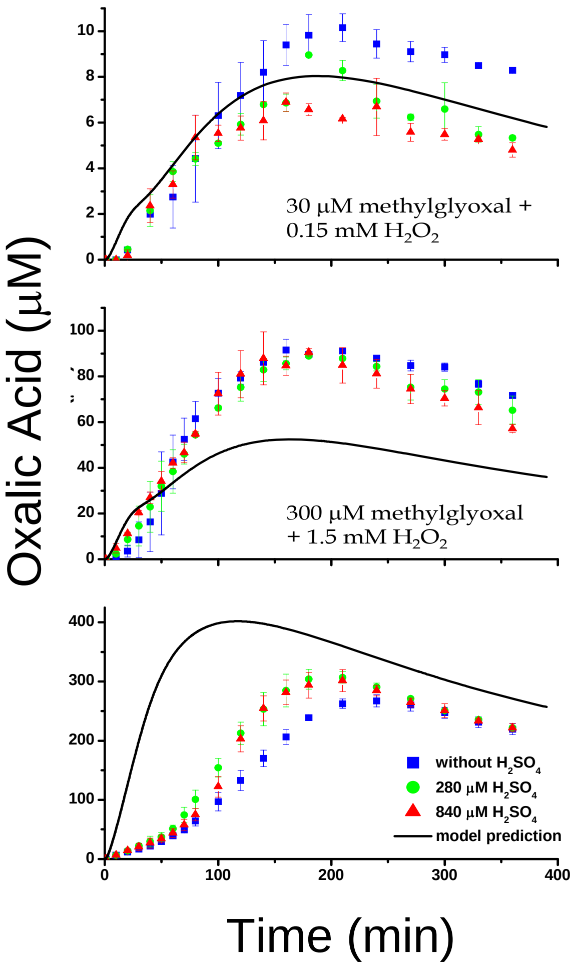
Ervens *GRL* 2008
Ervens *ACP* 2010

Model deviates from measurements at higher concentrations – what happens in wet aerosols?

Glyoxal



Methylglyoxal



Cloud relevant
~30 µM

300 µM

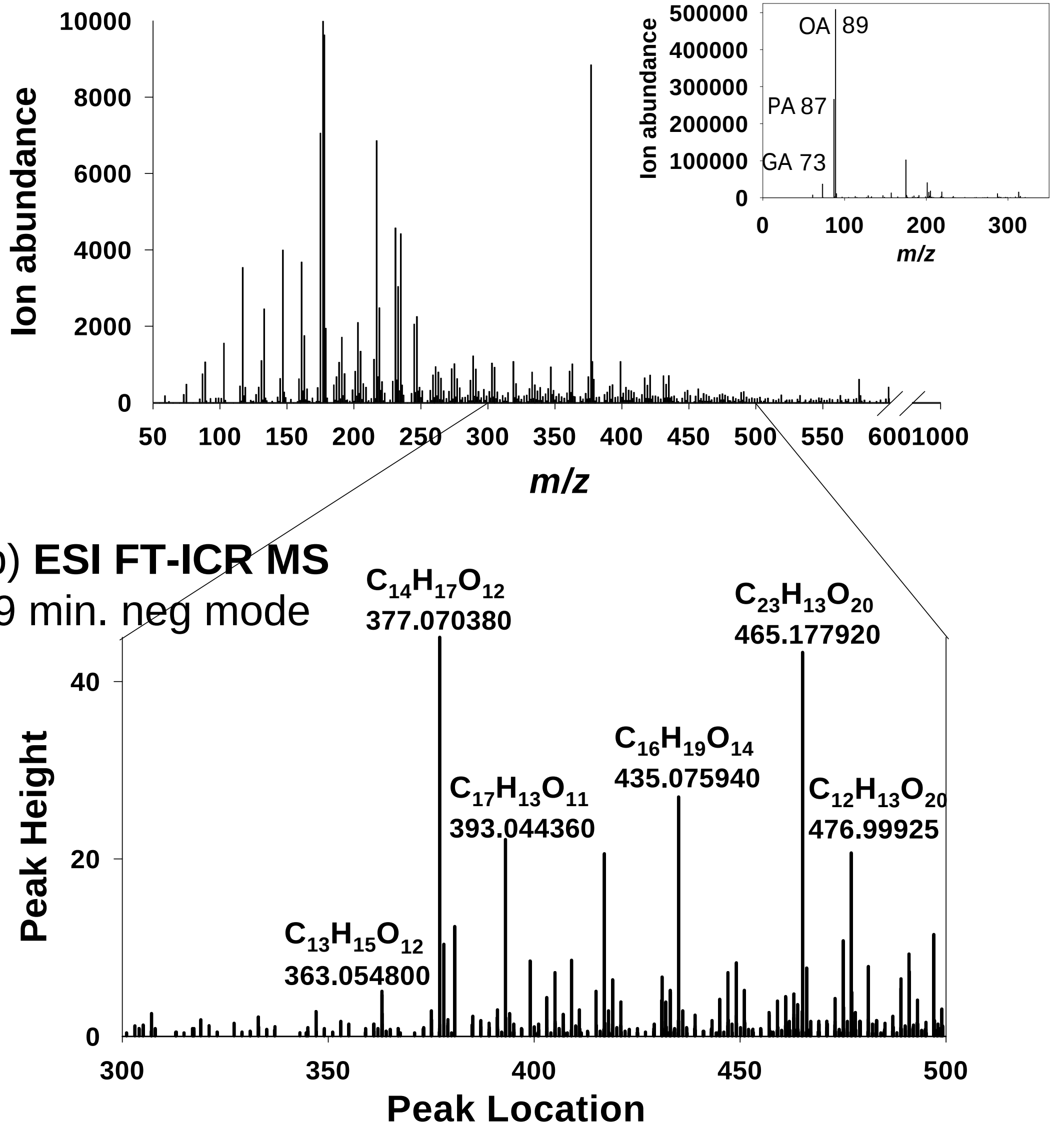
3000 µM

Aerosol relevant ~1-10 M

Methylglyoxal (1mM) + ·OH

- High MW products
- O/C ~ 1
- Not seen in std mix (not ESI artifact)
- Not in controls (·OH involved)

Ultra high resolution FT-ICR MS (9.4 T) provides exact elemental comp. > *m/z* 300



(a) **ESI-MS**
69 min. neg mode

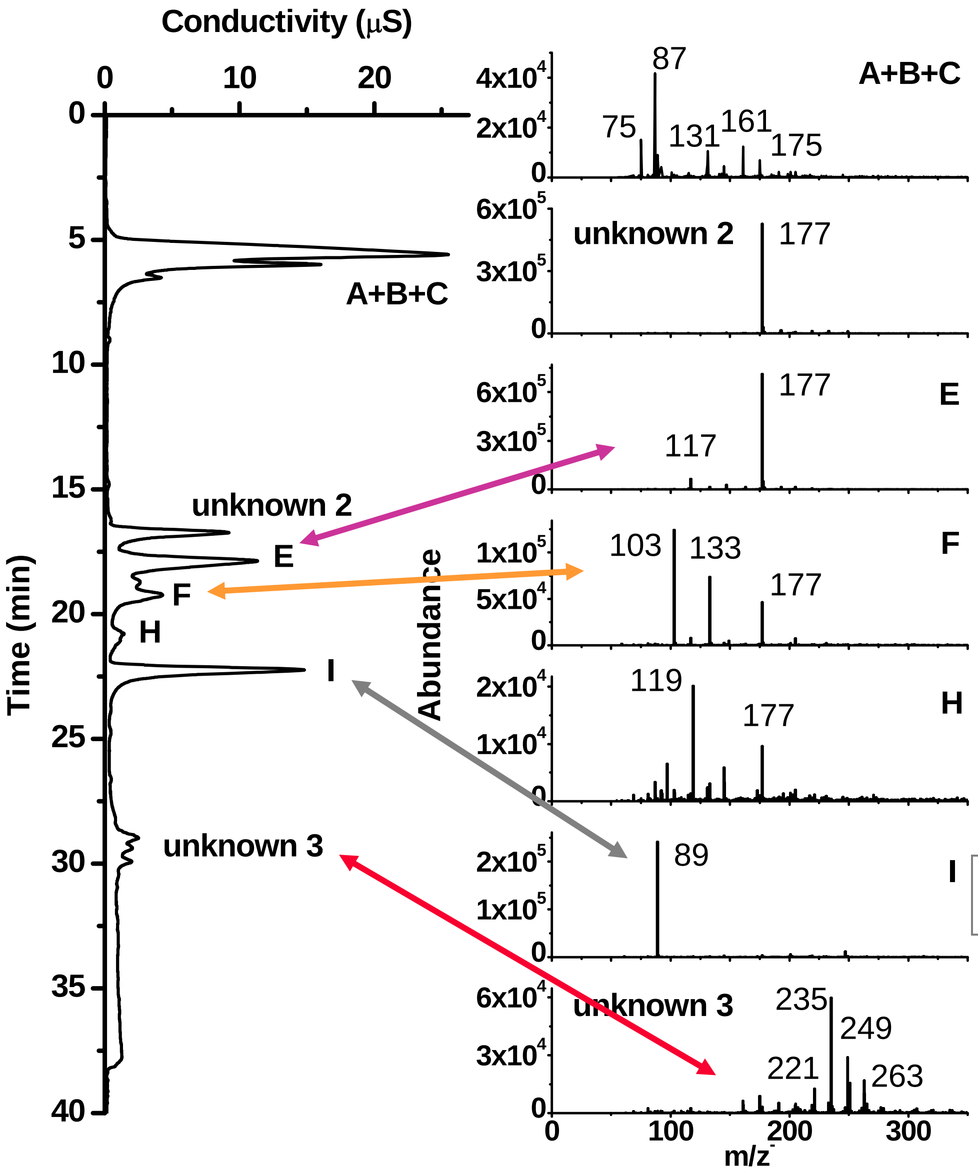
(b) **ESI FT-ICR MS**
69 min. neg mode

*Electrospray ionization Fourier transform-ion cyclotron resonance mass spectrometry

Altieri *AE* 2008

Chemistry at Higher Concentrations—Methylglyoxal

Formation of higher C# products



RT of Succinic acid (m/z$^-$ 117)

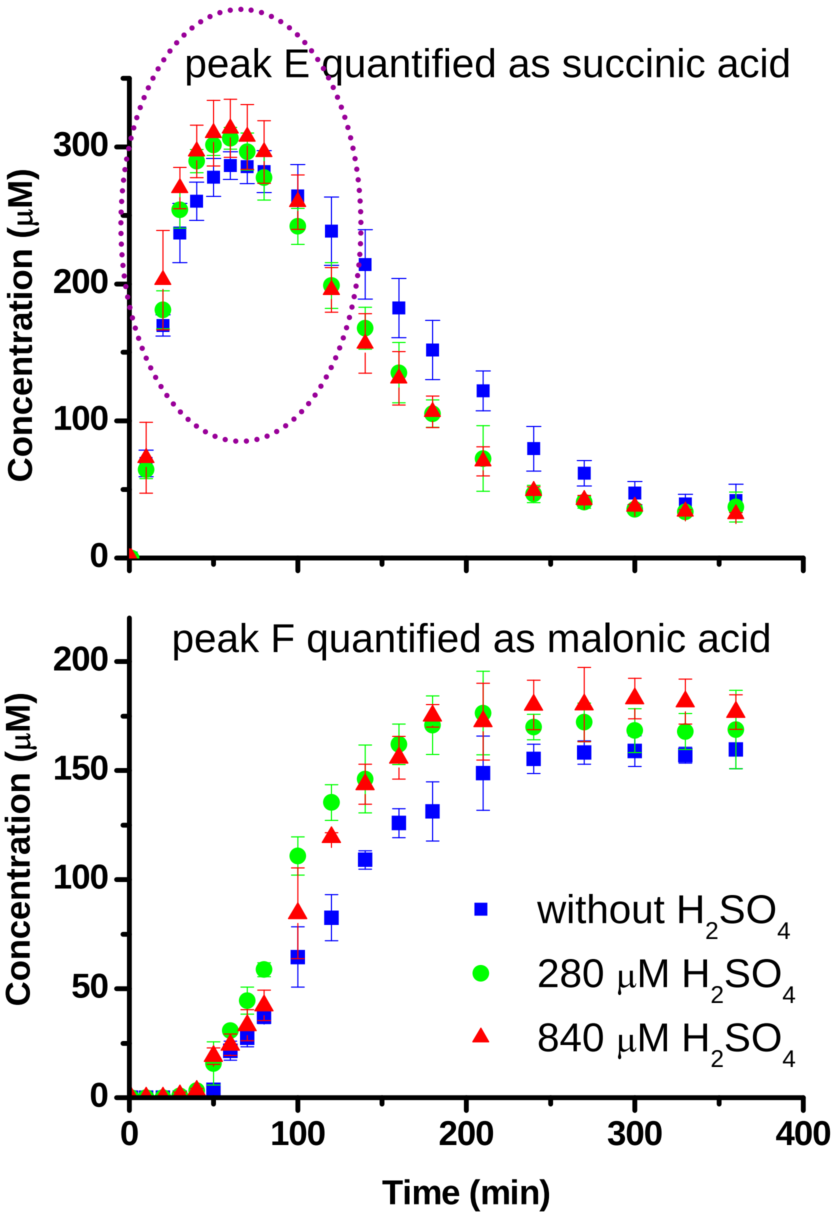
RT of Malonic acid (m/z$^-$ 103)

Oxalic acid (peak I, m/z$^-$ 89)

Higher-MW ions

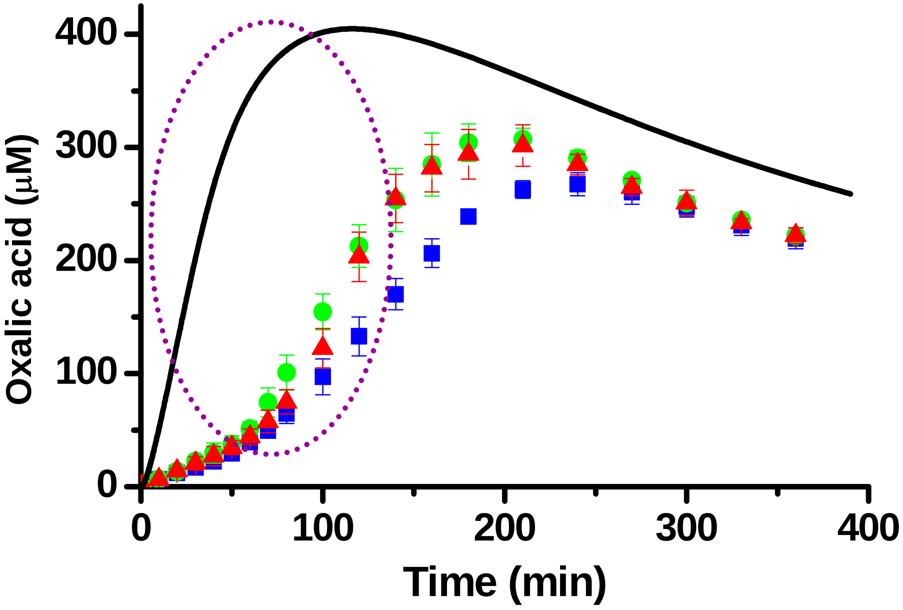
Tan *AE*, 2010

Chemistry at Higher Concentrations—Methylglyoxal

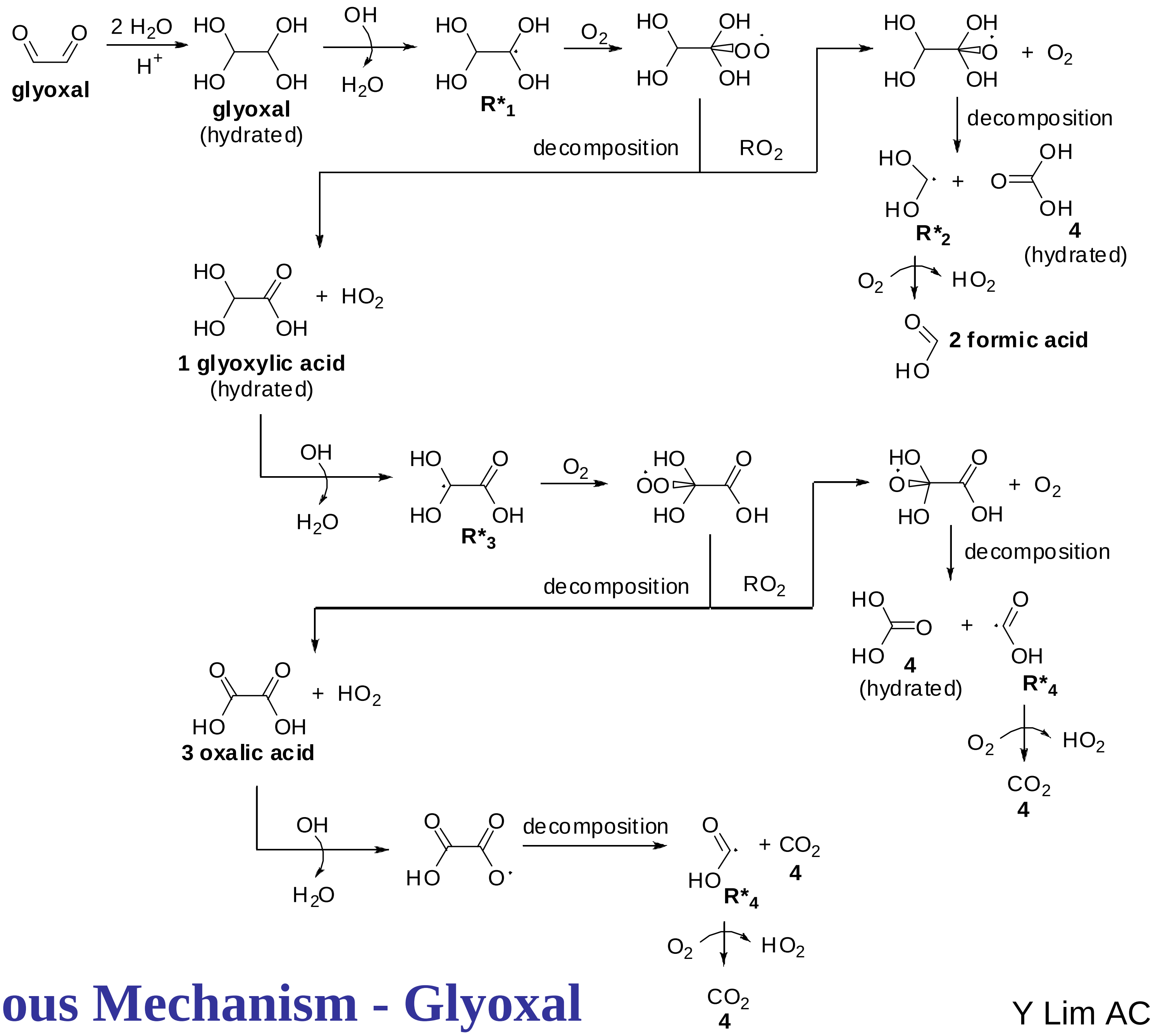


Larger acids are important products at higher concentrations.

Formation of higher C# products suggests radical-radical reactions



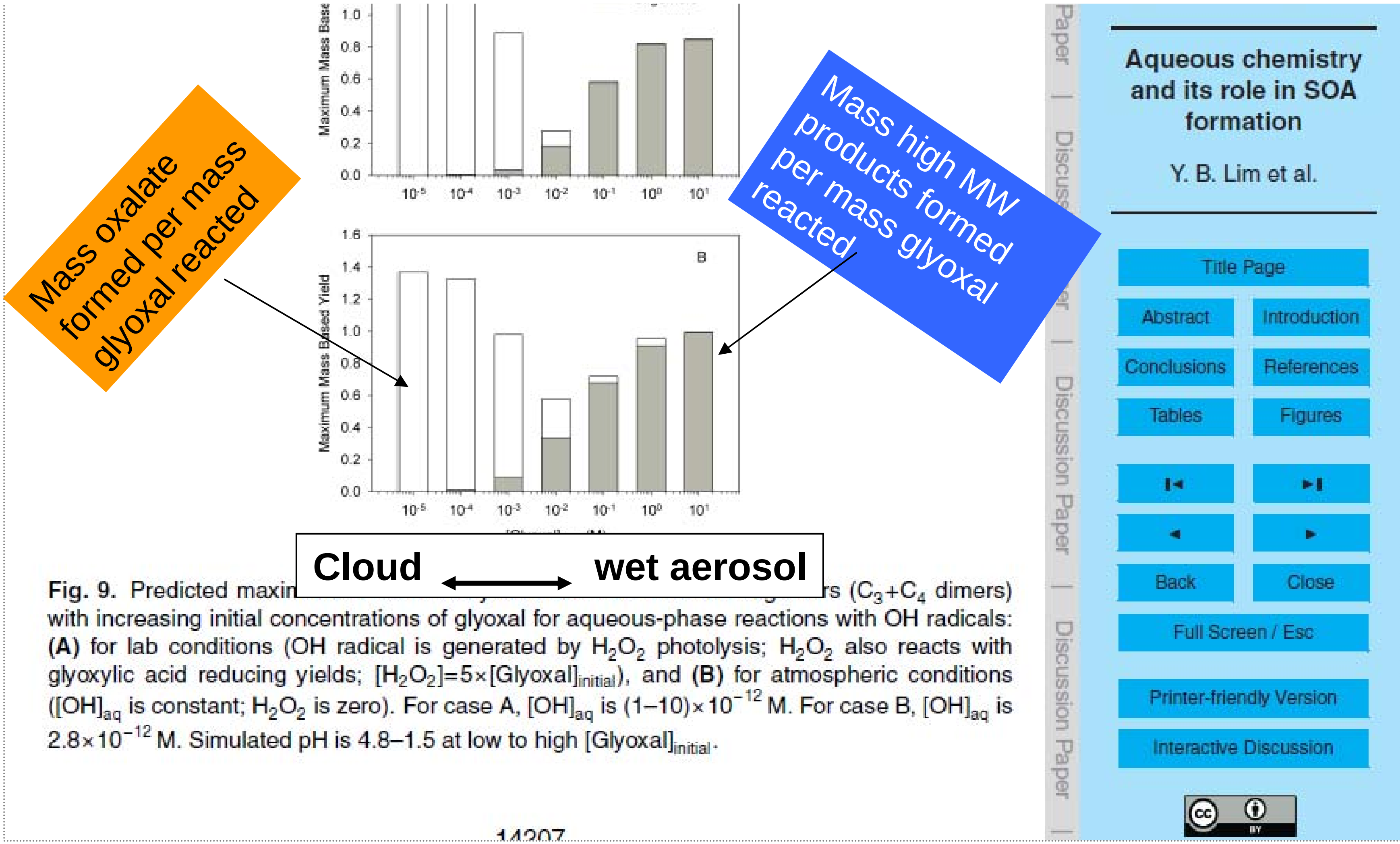
(Tan AE 2010)



Aqueous Mechanism - Glyoxal

Y Lim ACPD 2010

Model produces oxalate at cloud-relevant concentrations and oligomers at aerosol-relevant glyoxal concentrations (OH radical = 10^{-12} M)



Mass oxalate formed per mass glyoxal reacted

Mass high MW products formed per mass glyoxal reacted

Cloud ⟷ wet aerosol

Fig. 9. Predicted maxin rs (C_3+C_4 dimers) with increasing initial concentrations of glyoxal for aqueous-phase reactions with OH radicals: **(A)** for lab conditions (OH radical is generated by H_2O_2 photolysis; H_2O_2 also reacts with glyoxylic acid reducing yields; $[H_2O_2]=5\times[\text{Glyoxal}]_{\text{initial}}$), and **(B)** for atmospheric conditions ($[OH]_{aq}$ is constant; H_2O_2 is zero). For case A, $[OH]_{aq}$ is $(1\text{–}10)\times10^{-12}$ M. For case B, $[OH]_{aq}$ is 2.8×10^{-12} M. Simulated pH is 4.8–1.5 at low to high $[\text{Glyoxal}]_{\text{initial}}$.

14207

Y Lim ACPD 2010

Chemistry in wet aerosols – complex

- Photolysis and photooxidation reactions
- Reactions of organics with ammonium and amines to form organic-nitrogen compounds
- Reactions of organics with sulfate to form organic-sulfates
- Acid and ammonium catalyzed oligomerization

Investigators include:

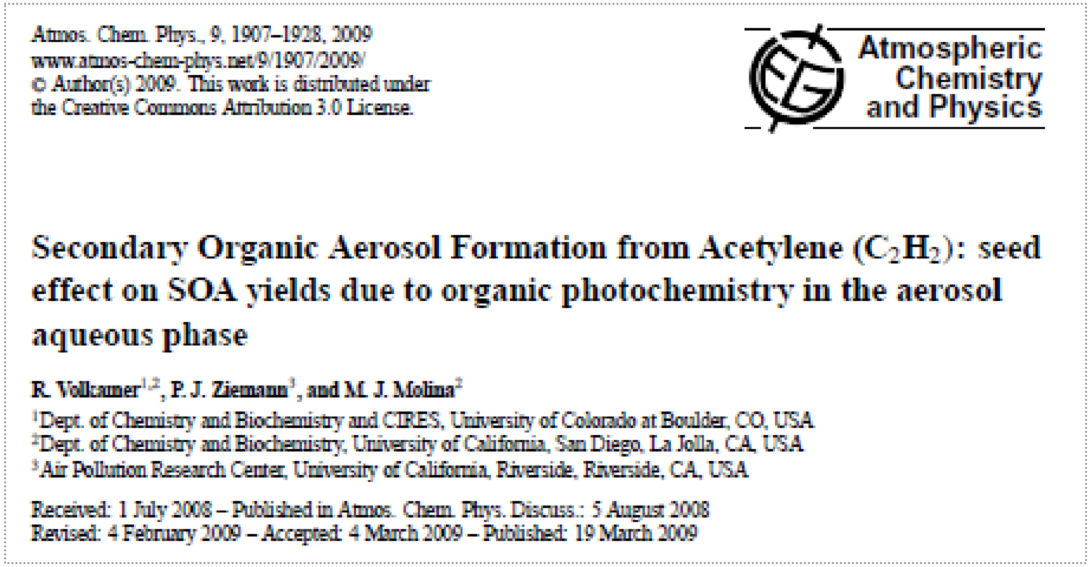
Anastasio, Claeys, Cordova, de Haan, Flagan, Galloway, Grgic, Guzman, Hoffmann, Jimenez, Keutsch, Liu, Maenhaut, Michaud, McNeill, Monod, Noziere, Sareen, Seinfeld, Shapiro**,** Sun, Tolbert, Volkamer, Wortham, Yasmeen, Zhang

SOA formation from glyoxal increases with LWC

SOA formation faster with OH radical (light)

Volkamer ACP 2009

(Seed: ammonium bisulfate + humic acid salt; acetylene; hydrogen peroxide; light/dark)



Atmos. Chem. Phys., 9, 1907–1928, 2009
www.atmos-chem-phys.net/9/1907/2009/
© Author(s) 2009. This work is distributed under
the Creative Commons Attribution 3.0 License.

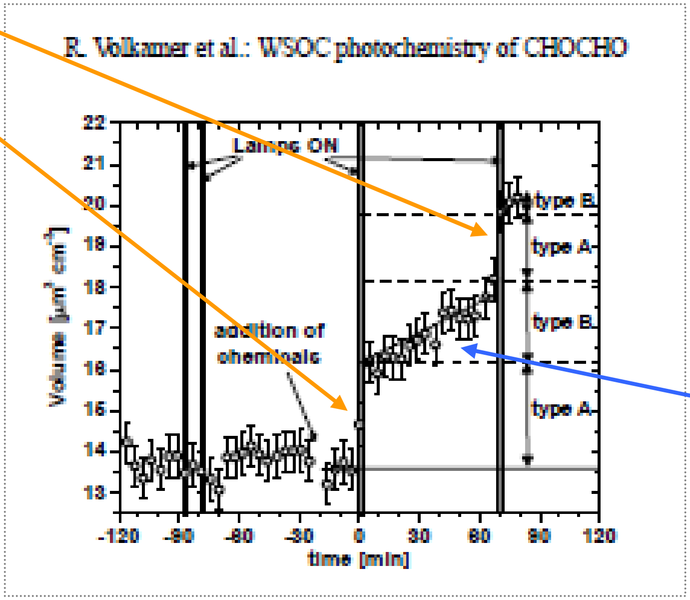
Atmospheric Chemistry and Physics

Secondary Organic Aerosol Formation from Acetylene (C_2H_2): seed effect on SOA yields due to organic photochemistry in the aerosol aqueous phase

R. Volkamer[1,2], P. J. Ziemann[3], and M. J. Molina[2]

[1]Dept. of Chemistry and Biochemistry and CIRES, University of Colorado at Boulder, CO, USA
[2]Dept. of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA, USA
[3]Air Pollution Research Center, University of California, Riverside, Riverside, CA, USA

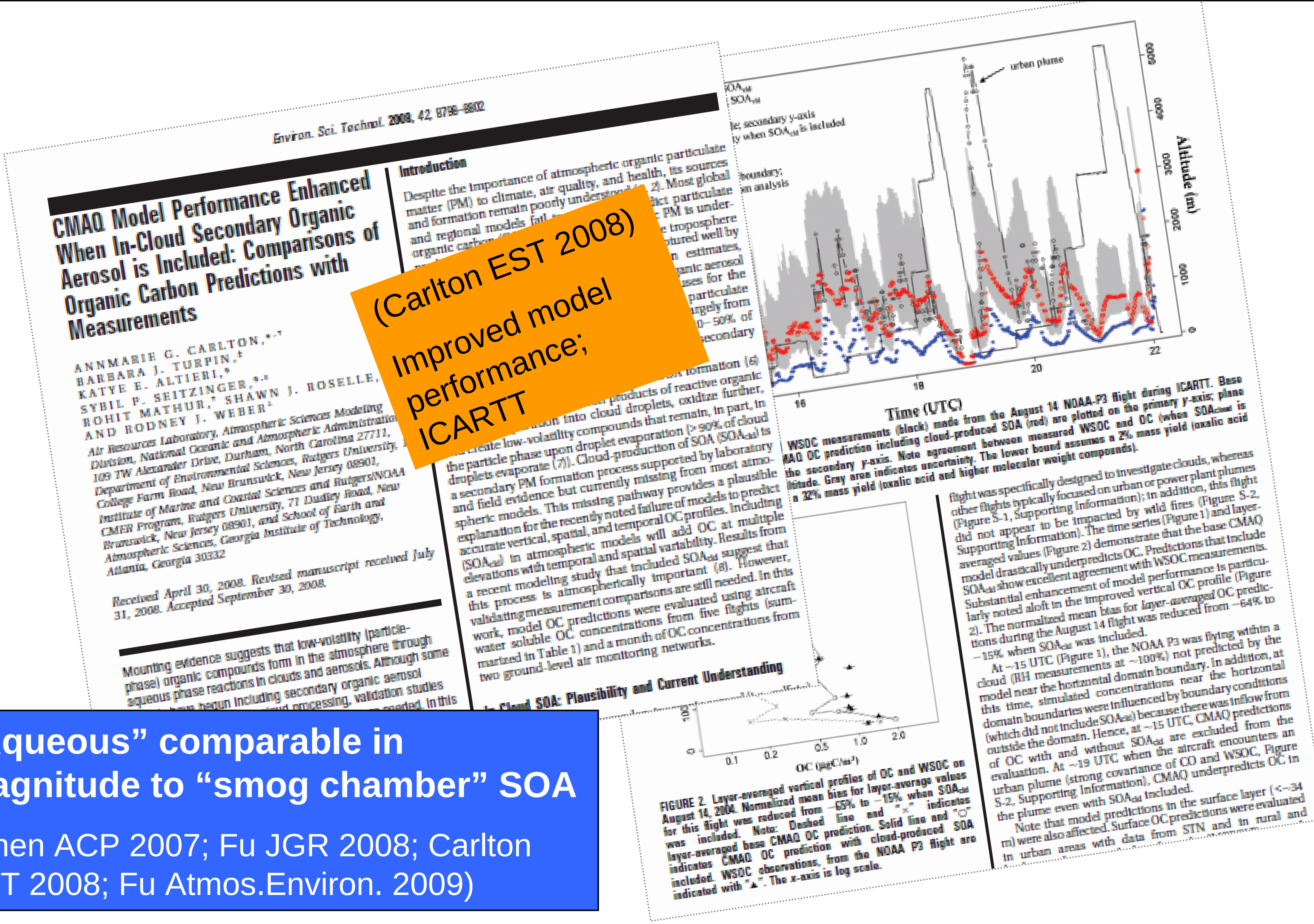
Received: 1 July 2008 – Published in Atmos. Chem. Phys. Discuss.: 5 August 2008
Revised: 4 February 2009 – Accepted: 4 March 2009 – Published: 19 March 2009



R. Volkamer et al.: WSOC photochemistry of CHOCHO

Dark reaction

SOA through cloud processing now in CMAQ (yields)



Environ. Sci. Technol. 2008, 42, 8798–8802

CMAQ Model Performance Enhanced When In-Cloud Secondary Organic Aerosol is Included: Comparisons of Organic Carbon Predictions with Measurements

ANNMARIE G. CARLTON, BARBARA J. TURPIN, KATYE E. ALTIERI, SYBIL P. SEITZINGER, ROHIT MATHUR, SHAWN J. ROSELLE, AND RODNEY J. WEBER

(Carlton EST 2008)

Improved model performance; ICARTT

“Aqueous” comparable in magnitude to “smog chamber” SOA

(Chen ACP 2007; Fu JGR 2008; Carlton EST 2008; Fu Atmos.Environ. 2009)

Overview

(Lim et al., ACPD 2010)

- Predictive models capture organic aerosol poorly
    - **aqueous SOA precursors different** (Volkamer ACP 2009)
    - **improved with “aqueous” SOA** (Carlton EST 2008)

- Atmospheric O/C > smog chamber O/C (Aiken EST 2008)
    - **atmos. OOA-LV = 0.8 – 1.0**
    - **atmos. OOA-SV = 0.5 – 0.6**
    - **sm. chamber SOA = 0.3 – 0.5**
    - **aqueous SOA = 1-2**

- Sometimes liquid water is more accessible than OM
    - **e.g., high humidities of eastern US**

- Atlanta - SOA is correlated with liquid water
    - **Atlanta** (Hennigan GRL 2008; Hennigan ACP 2009)

- Anthropogenic pollutants generate biogenic SOA
    - **higher yields for aqueous SOA from isoprene at high NOx** (Ervens GRL 2008)

Acknowledgements

Past/present Students, Postdocs

Ho Jin Lim
Katie Altieri
Yi Tan
Mark Perri
Yong Bin Lim
Diana Ortiz
Mary Moore
Anjuli Ramos
Phyllis Kuo
Jeff Kirkland

Support

U.S. EPA – STAR