

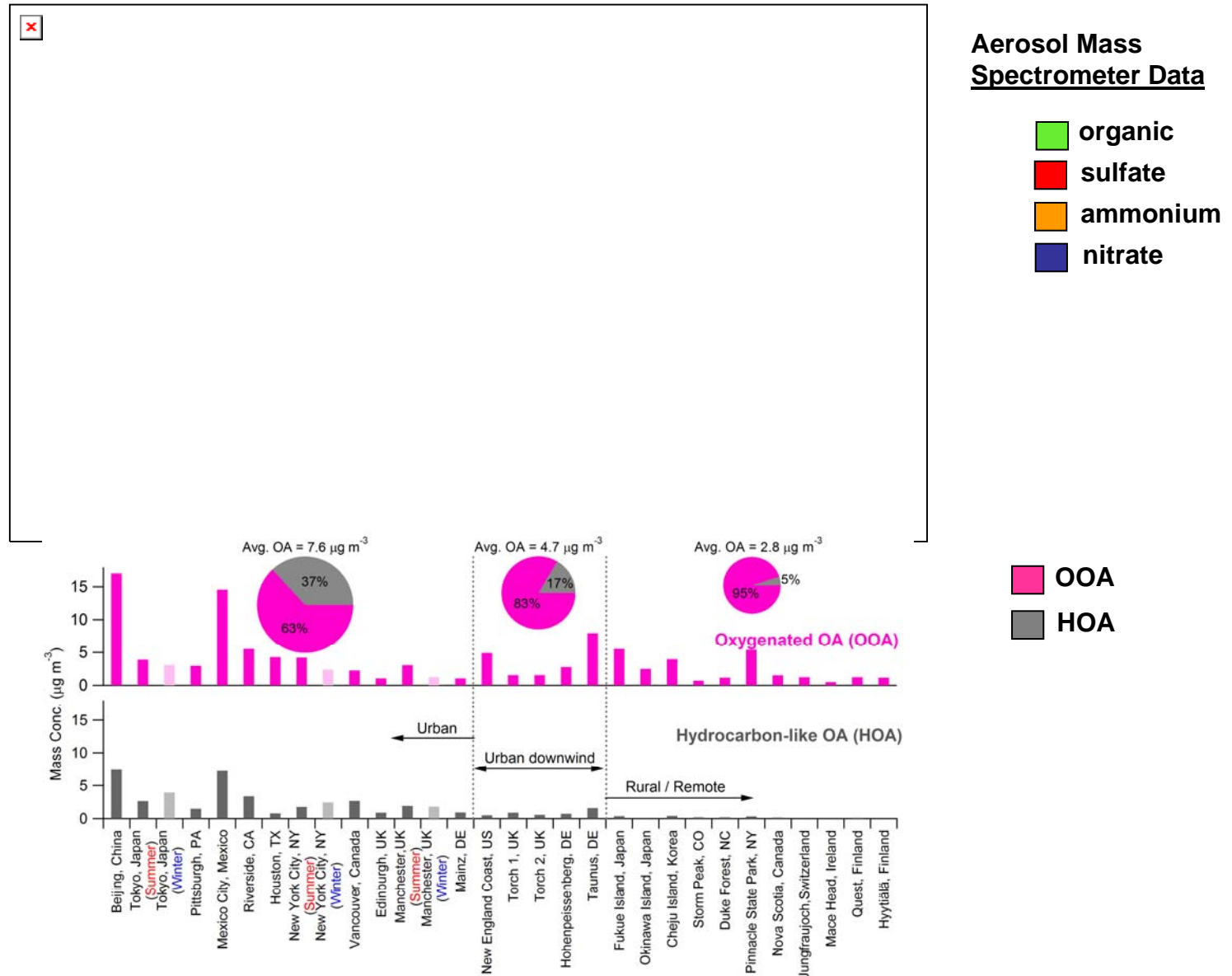
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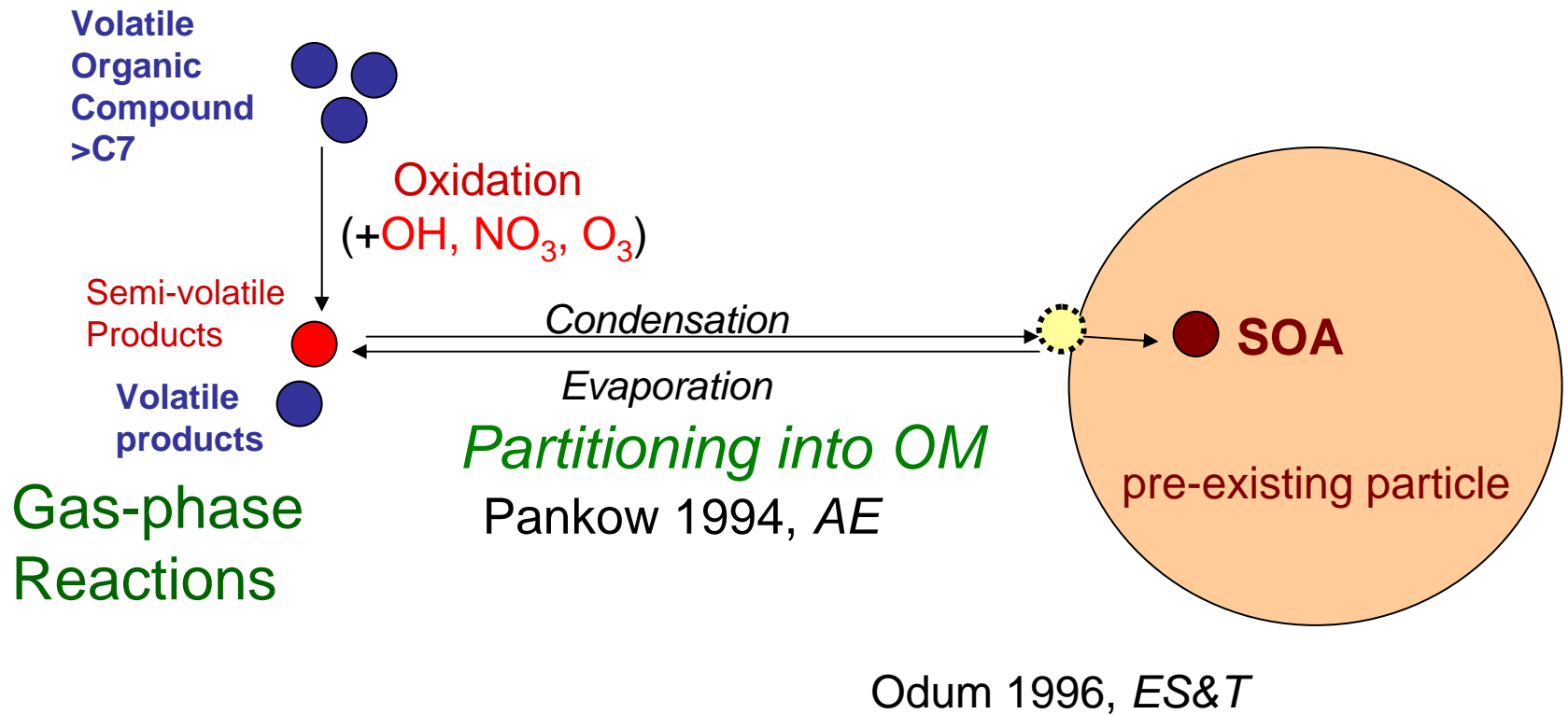
Improved Prediction of In-Cloud Biogenic SOA: Experiments and CMAQ Model Refinements

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SOA – a major fine particle constituent



Traditional "smog chamber" SOA



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)

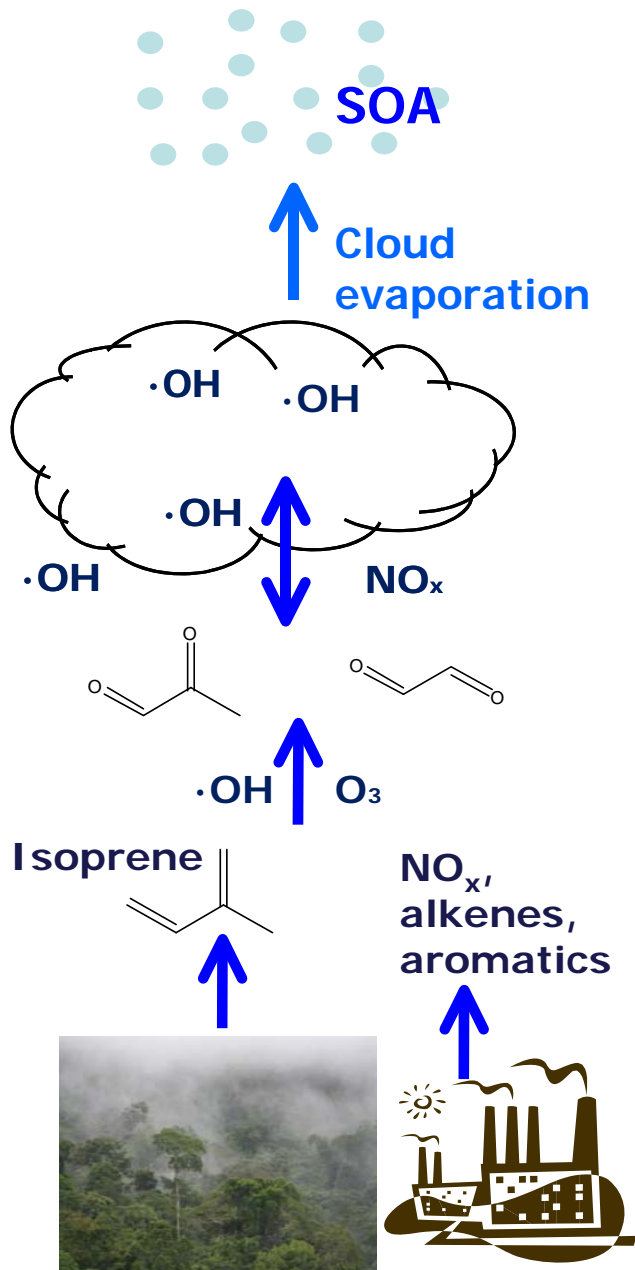
atmos. HOA = 0.06 – 0.1

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

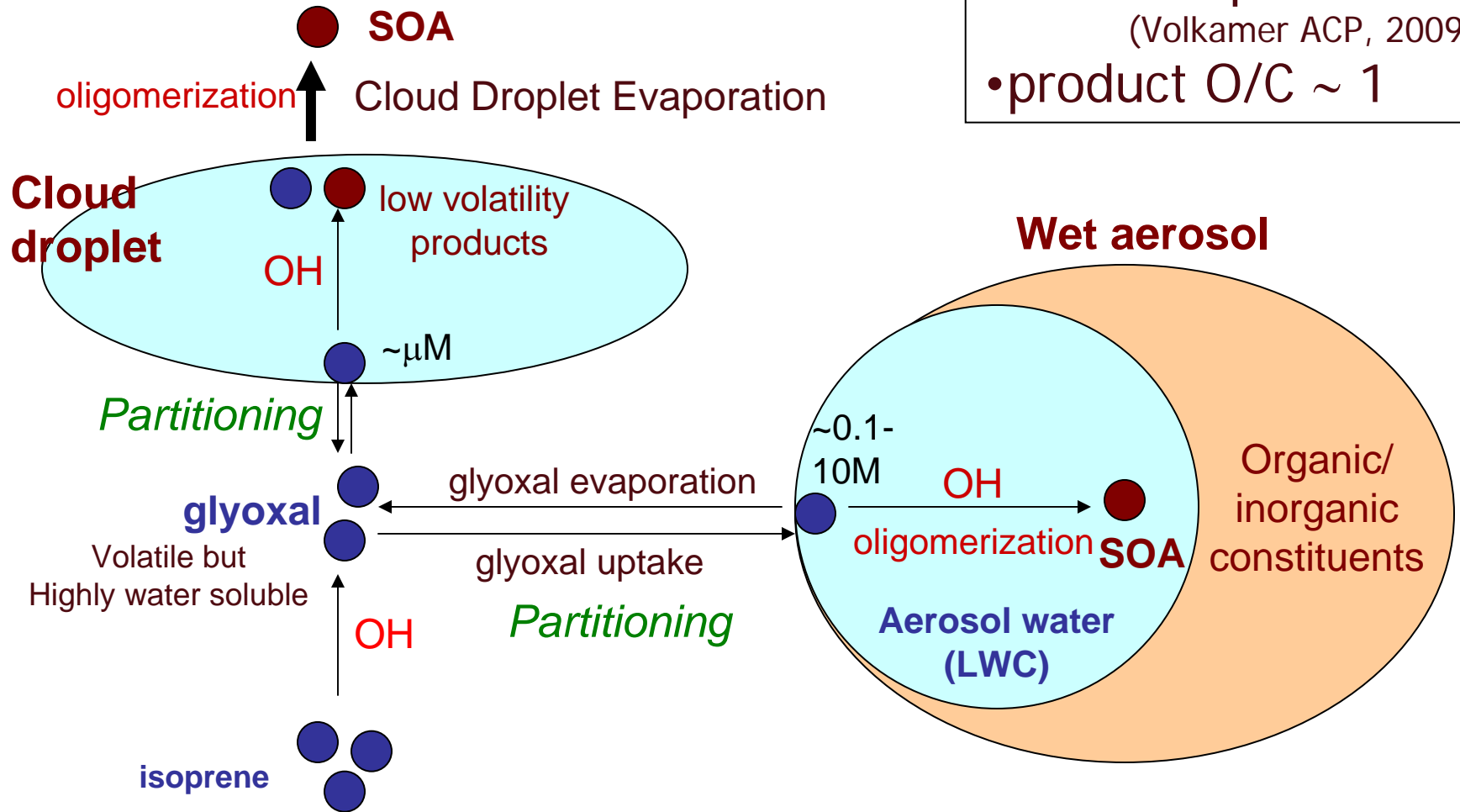
- Organic gases are oxidized forming water-soluble compounds.
- These partition into cloud droplets and react further (e.g., by ·OH).
- Cloud droplets evaporate, lower volatility products remain, forming SOA.

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*

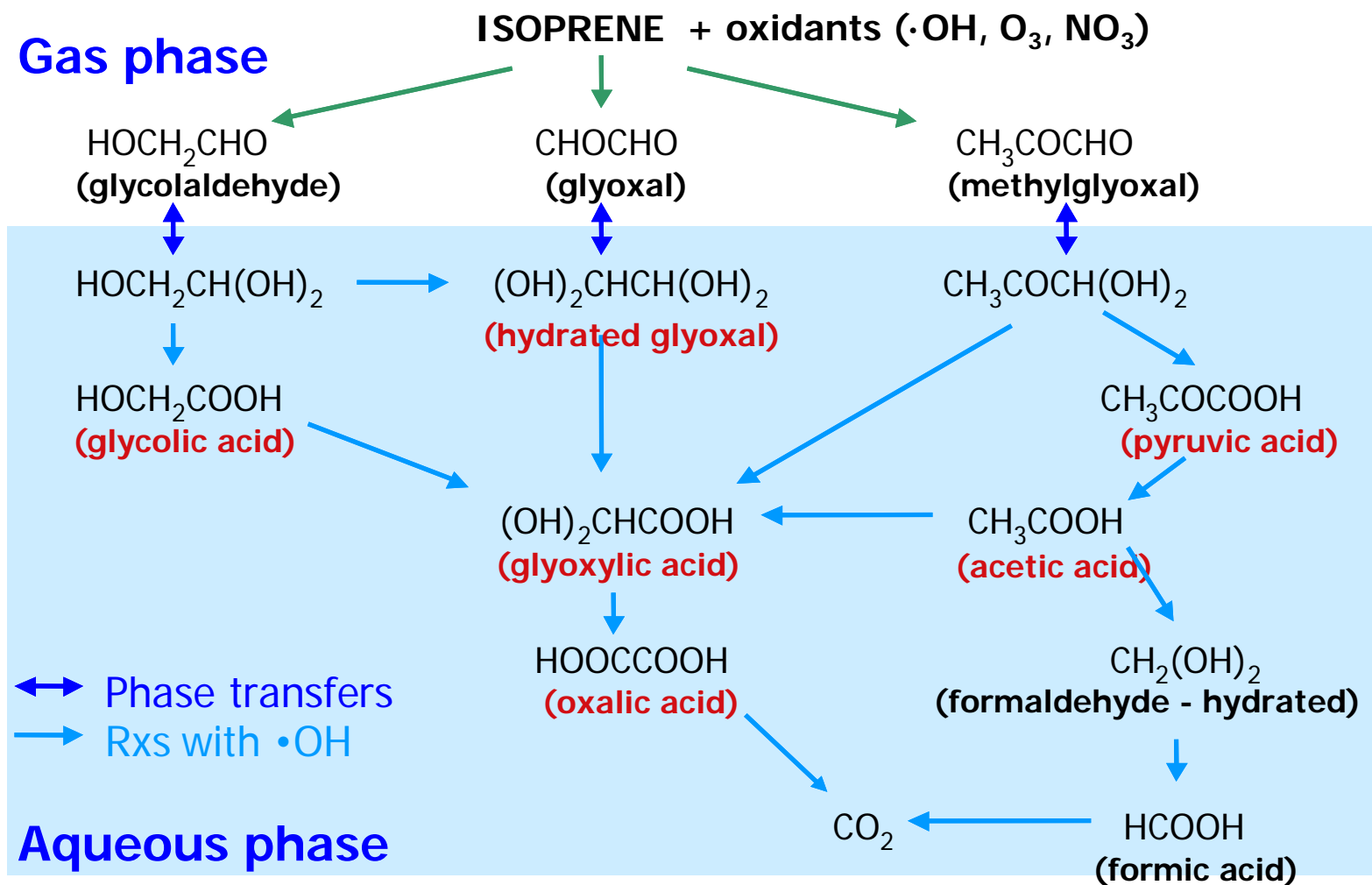


Implications

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

Previous research:

Major products of OH radical oxidation verified ($\geq 1\text{mM}$)



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?

Overall Goal:

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

Approach:

- Conduct aqueous experiments at cloud concentrations and \pm 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



Roles of NO_x in Aqueous SOA from Isoprene:

1. Gas phase formation of atmospheric oxidants
2. Gas phase formation of water soluble carbonyls
3. Aqueous NO₃ → 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

$\text{H}_2\text{O}_2 + h\nu \rightarrow \cdot\text{OH}$ ($\sim 10^{-12}$ M)

2-5 pH

$\pm \text{HNO}_3, \text{NH}_4$

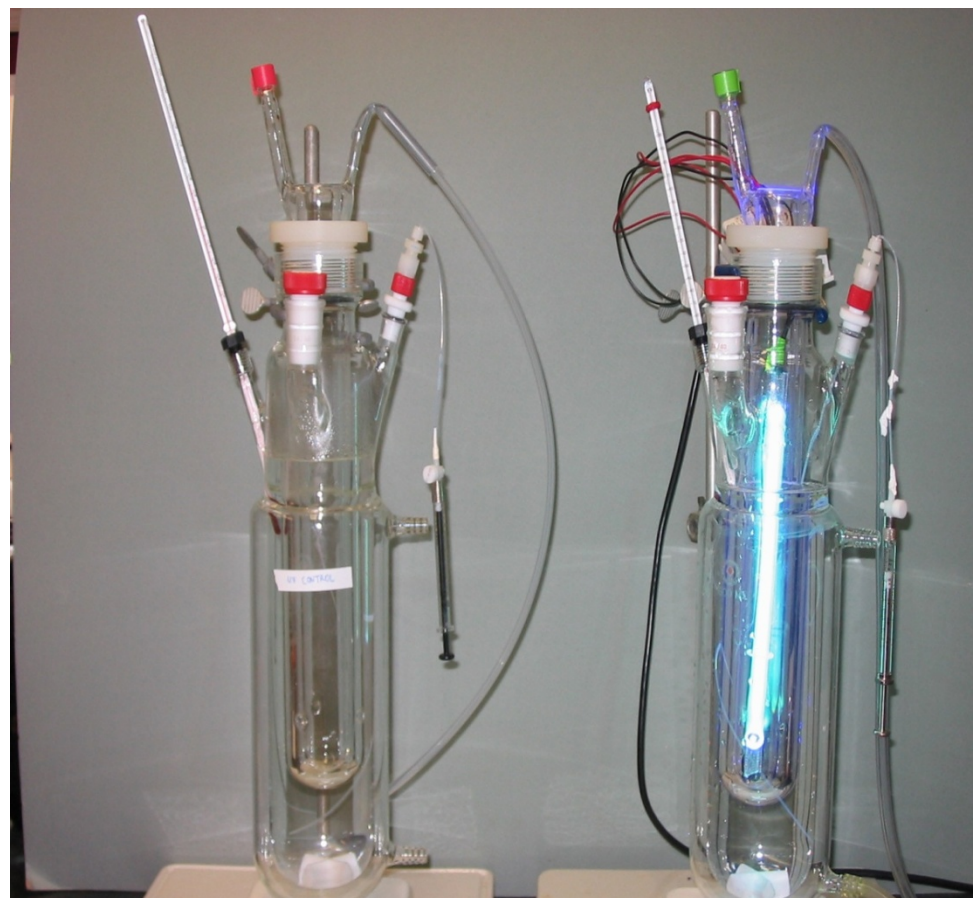
ORG: glyoxal, methylglyoxal

Controls

ORG+Prod+UV $\pm \text{HNO}_3, \text{NH}_4$

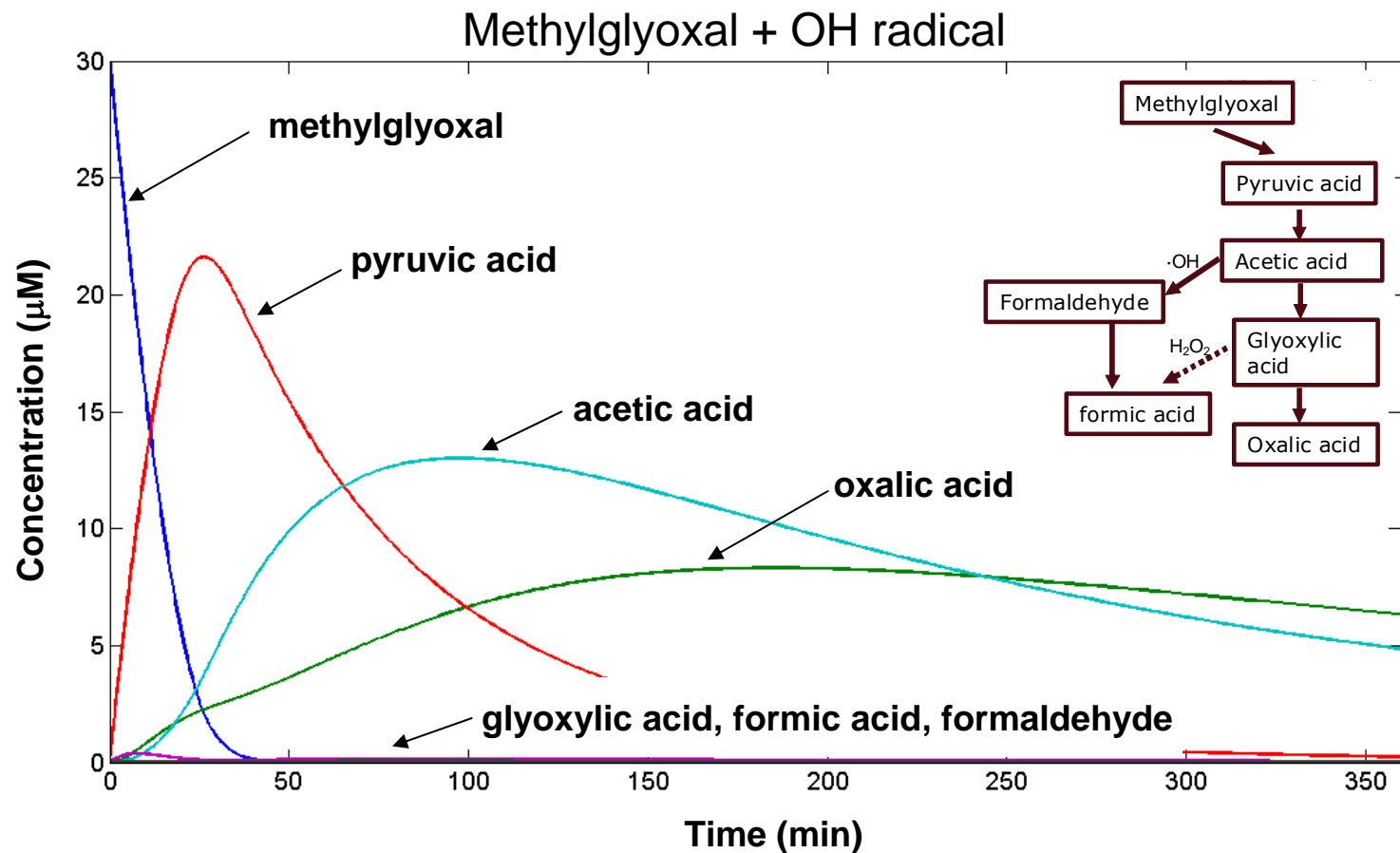
ORG+Prod+ H_2O_2 $\pm \text{HNO}_3, \text{NH}_4$

UV+ H_2O_2

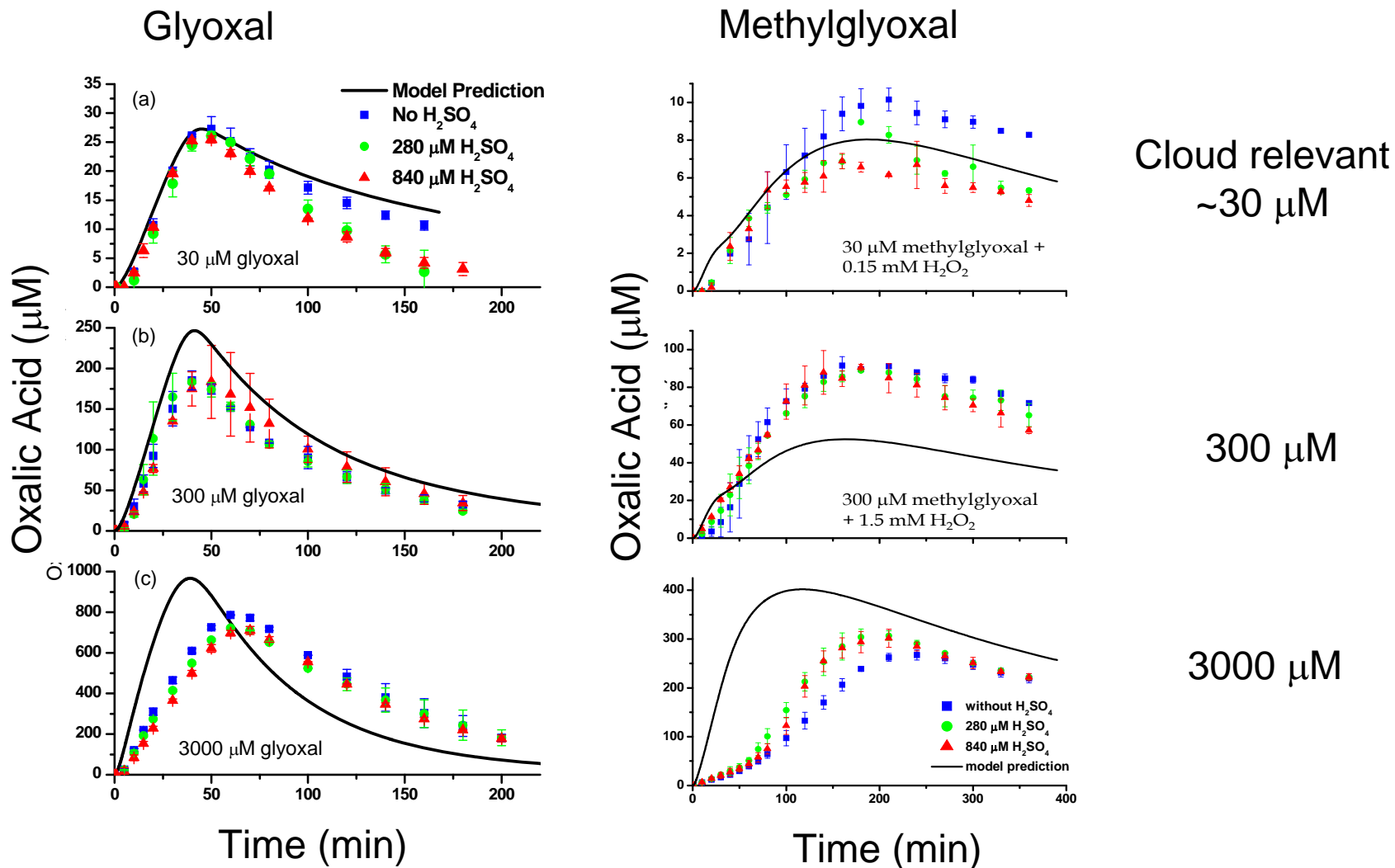


On-line ESI MS; IC-ESI-MS; FT-ICR MS; ESI-MS-MS,
UV or IC for organic acids, DOC for mass balance, H_2O_2

Precursor/products modeled in reaction vessel:

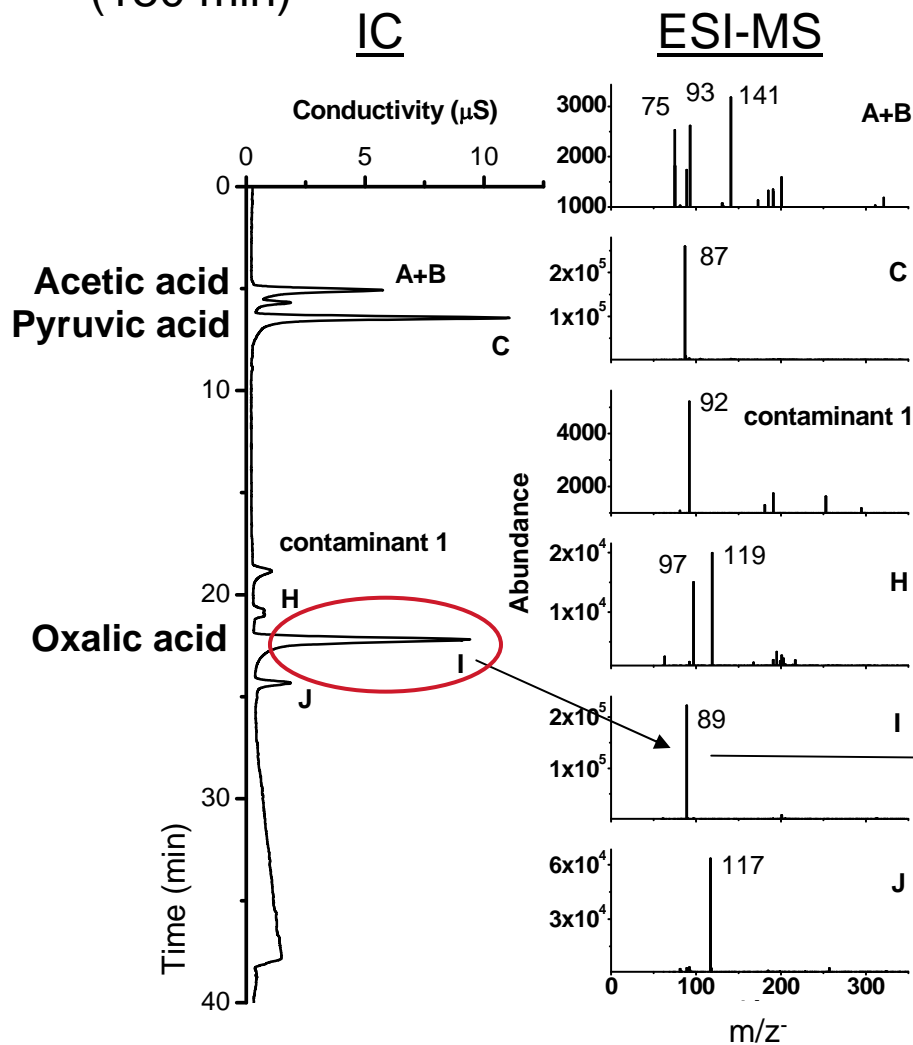


Dilute aqueous chemistry model reproduces oxalic, pyruvic acid and total organic carbon at 30 μM

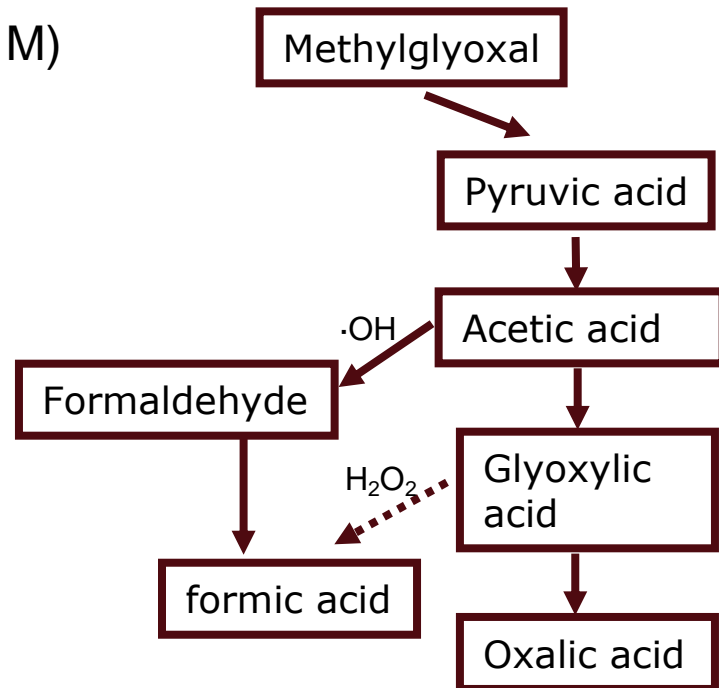


Oxalate formation verified with IC ESI-MS

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



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



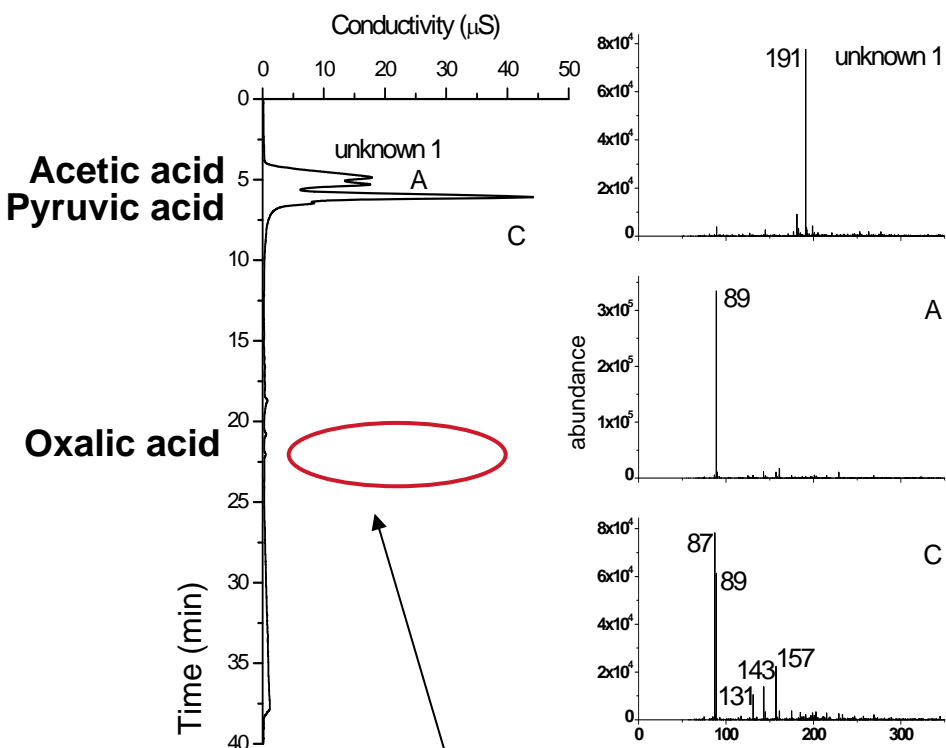
Methylglyoxal experiment with IC ESI-MS

Oxalic acid forms only in the presence of OH radical

Methylglyoxal (3000 μM) + UV
(180 min)

IC

ESI-MS

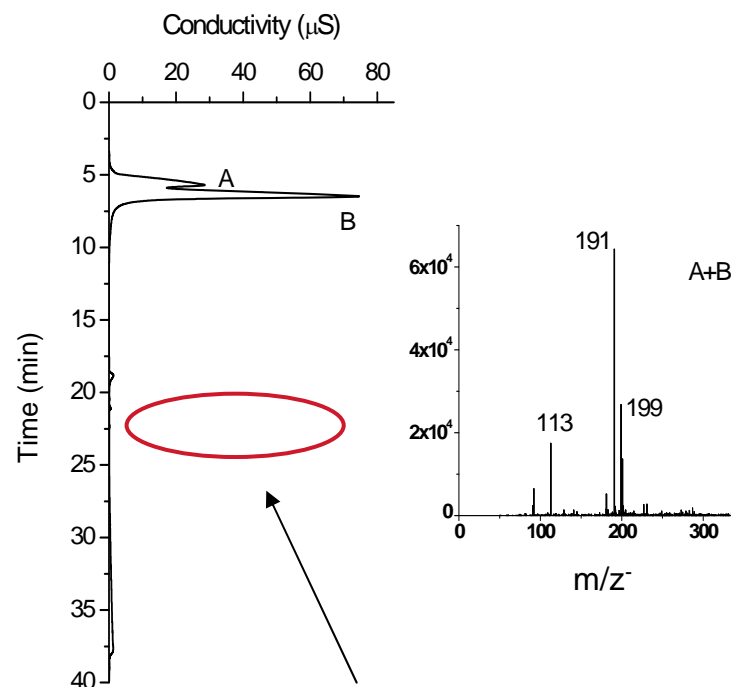


No oxalic acid forms in control experiments

Methylglyoxal (3000 μM) + H_2O_2

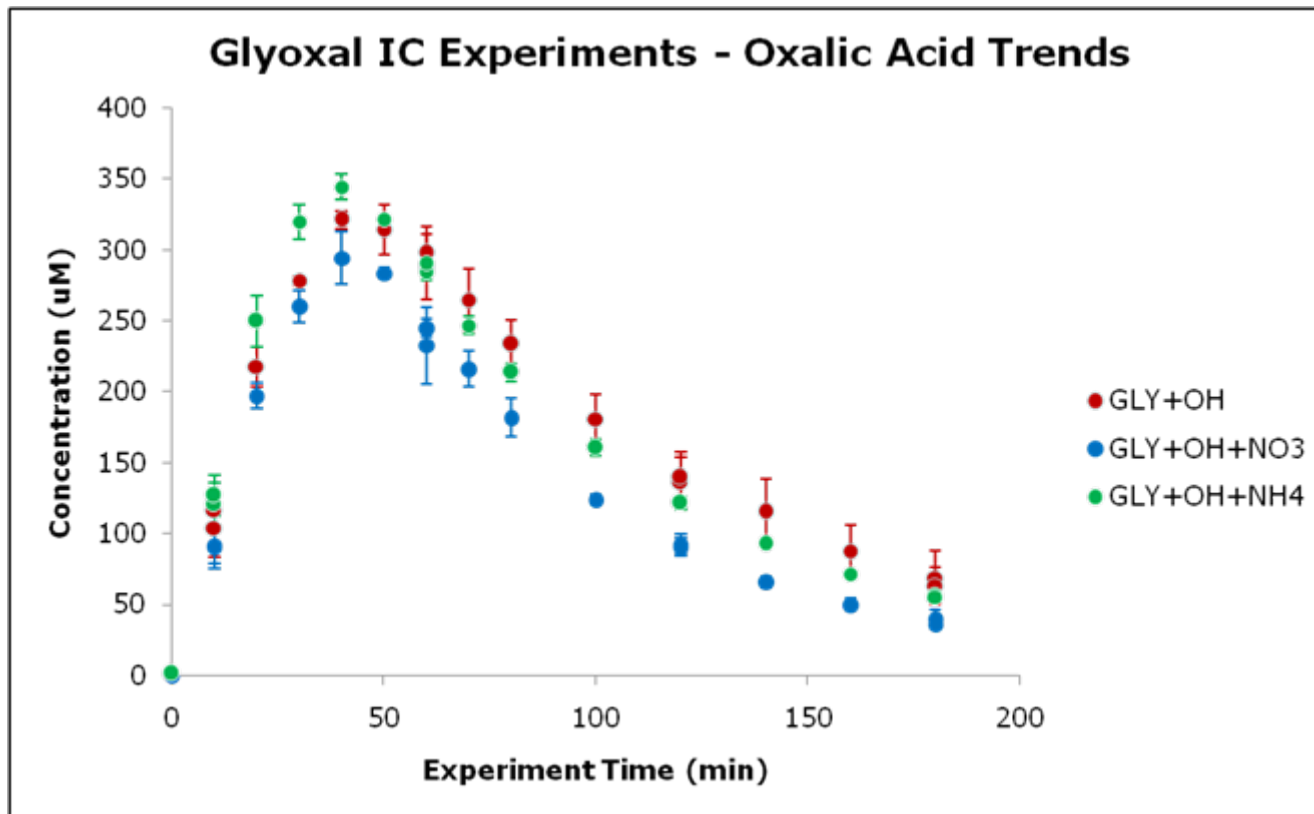
IC

ESI-MS



No oxalic acid forms in control experiments

Addition of HNO_3 (1.7 mM) or $(\text{NH}_4)_2\text{SO}_4$ (0.84 mM) to glyoxal (1 mM) and OH radical ($\sim 10^{-12}$ M)



Little effect on oxalate (slightly faster decay with nitric acid)

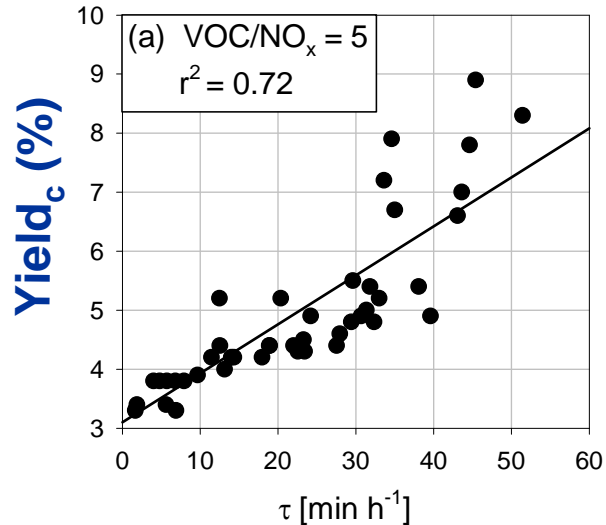
No change in nitrate or sulfate throughout the reaction

No discernable change in IC ESI-MS

Might still form enough organic-N to observe by FT-ICR MS

Impact of NO_x on SOA from isoprene through cloud proc.

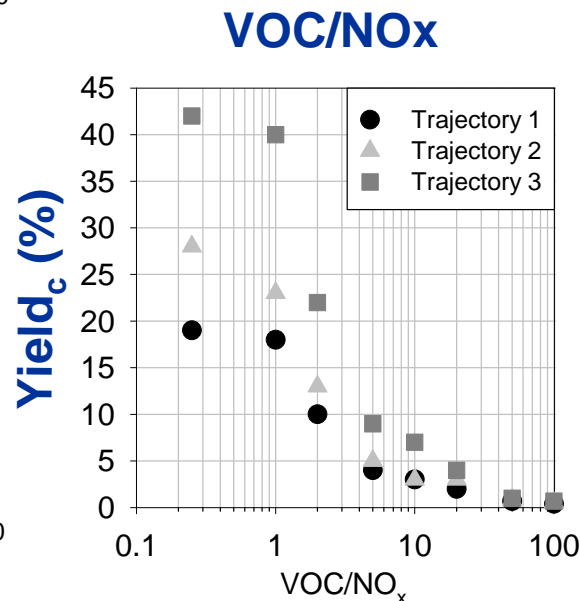
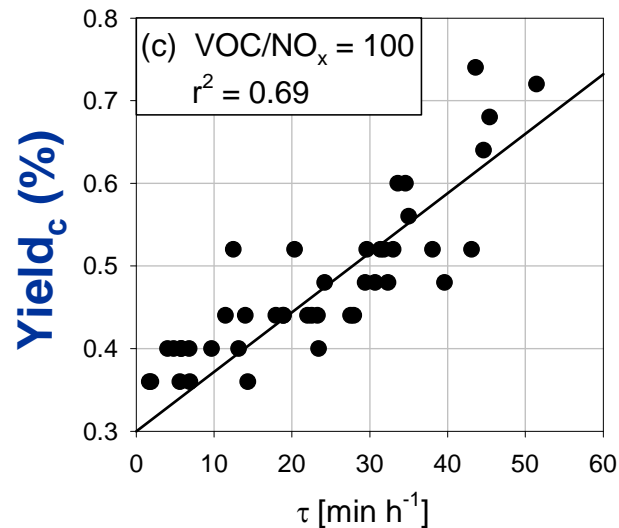
Cloud contact time



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

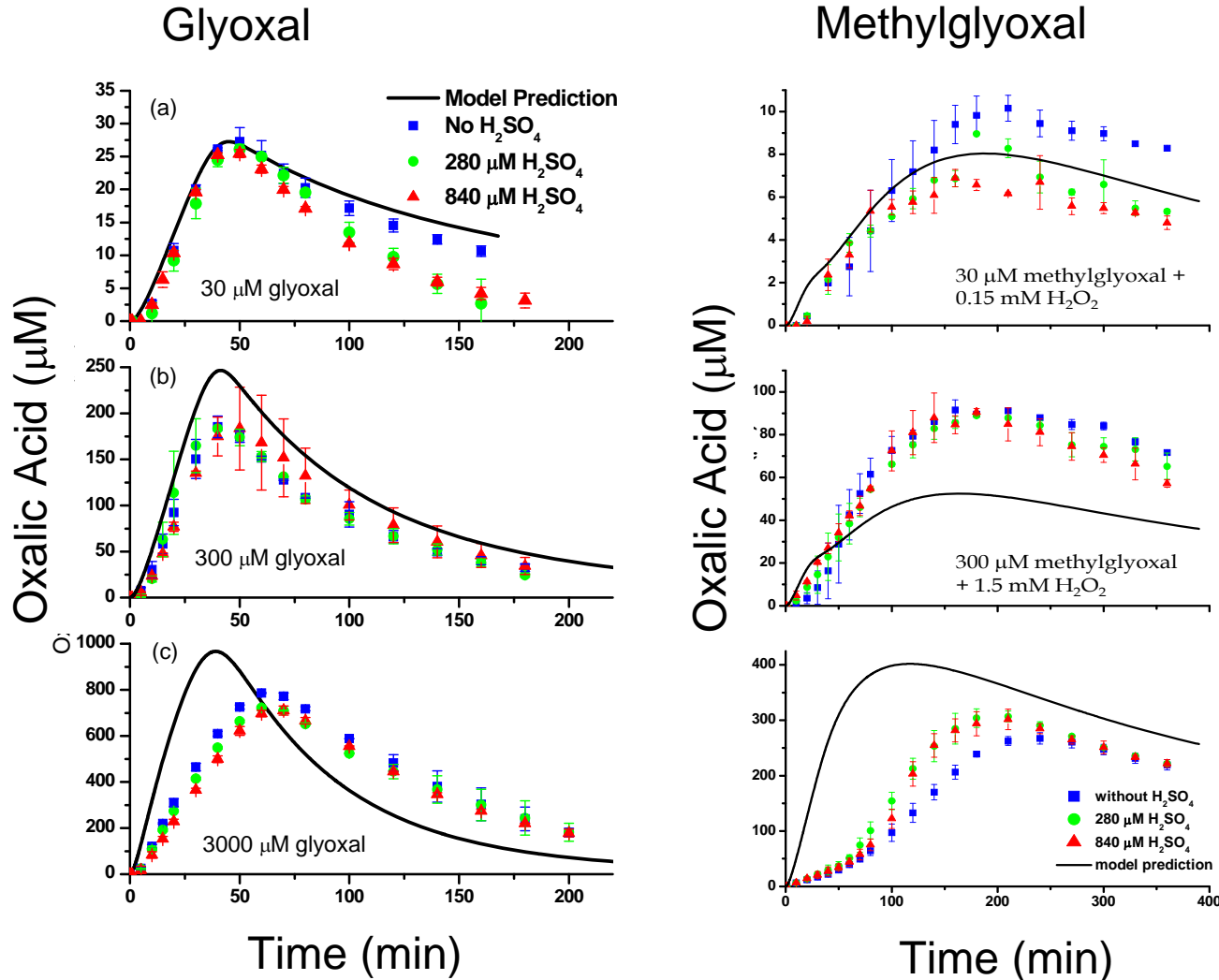
Yield (%) = $\frac{\text{mass C in SOA}}{\text{mass isoprene C}}$

Feingold microphys. cloud model



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

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



Cloud relevant
~30 µM

300 µM

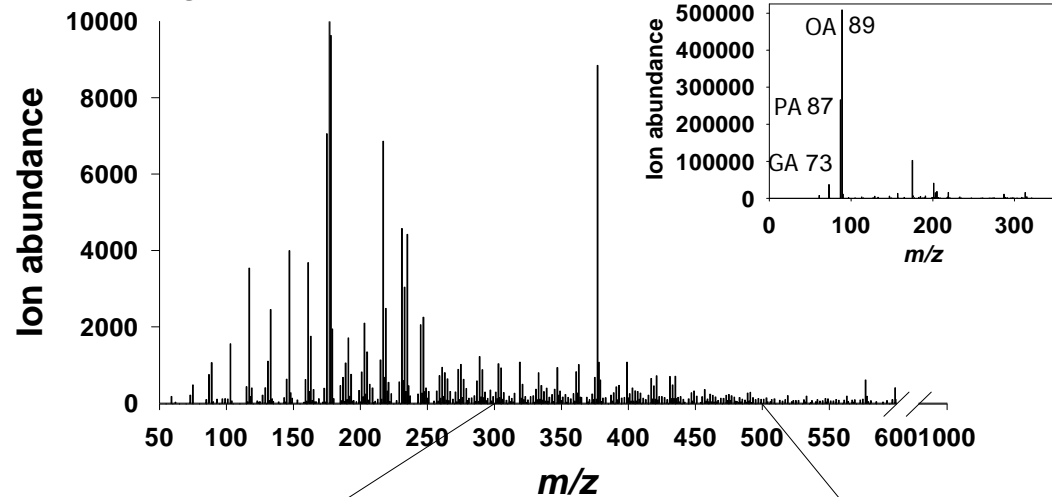
3000 µM

Aerosol relevant
~1-10 M

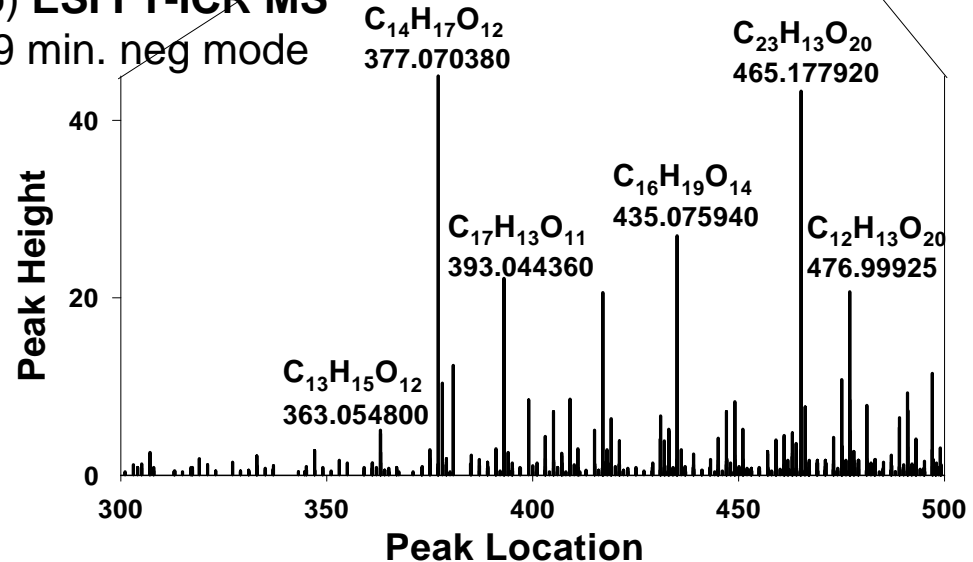
Methylglyoxal (1mM) + $\cdot\text{OH}$

- High MW products
- O/C ~ 1
- Not seen in std mix (not ESI artifact)
- Not in controls ($\cdot\text{OH}$ involved)

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



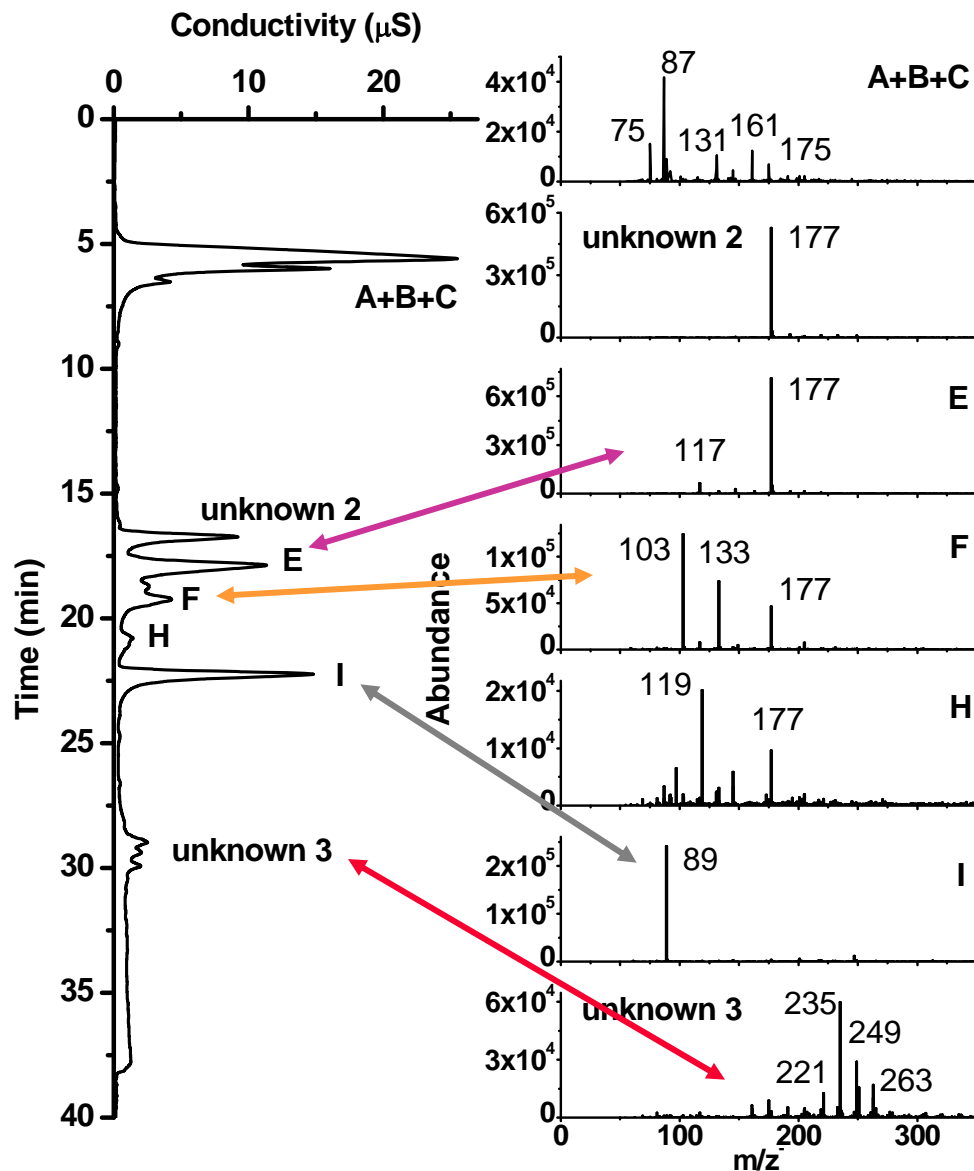
(b) **ESI FT-ICR MS**
69 min. neg mode



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

*Electrospray ionization Fourier transform-ion cyclotron resonance mass spectrometry

Chemistry at Higher Concentrations—Methylglyoxal



Formation of higher C# products

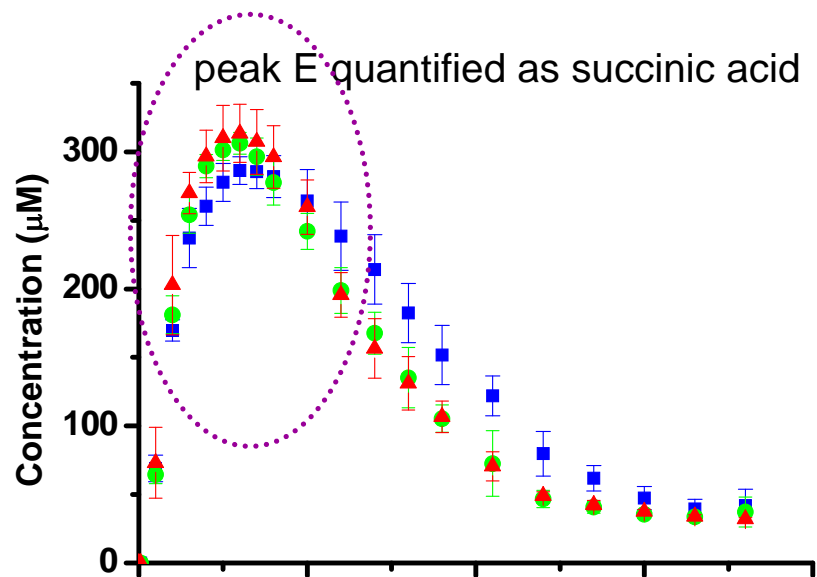
RT of Succinic acid (m/z- 117)

RT of Malonic acid (m/z- 103)

Oxalic acid (peak I, m/z 89)

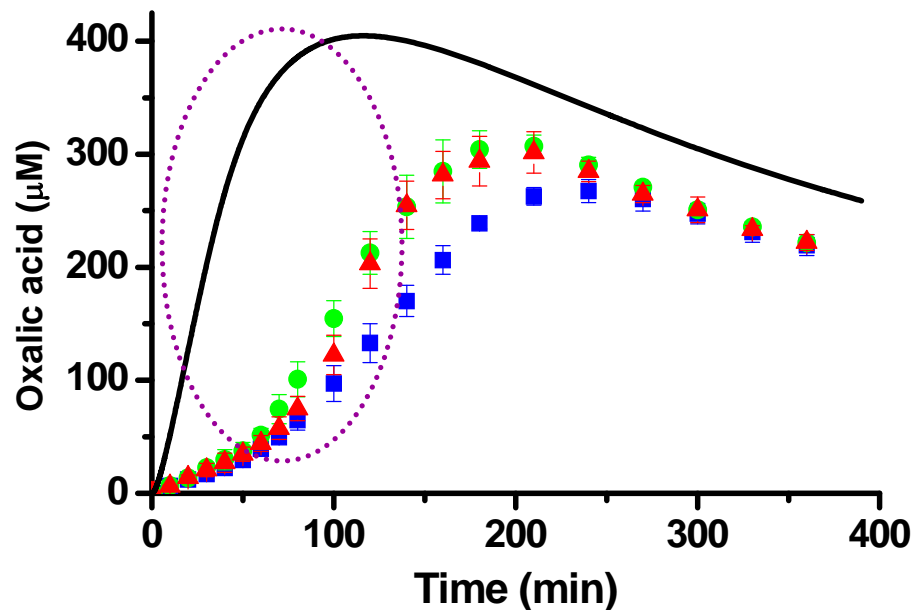
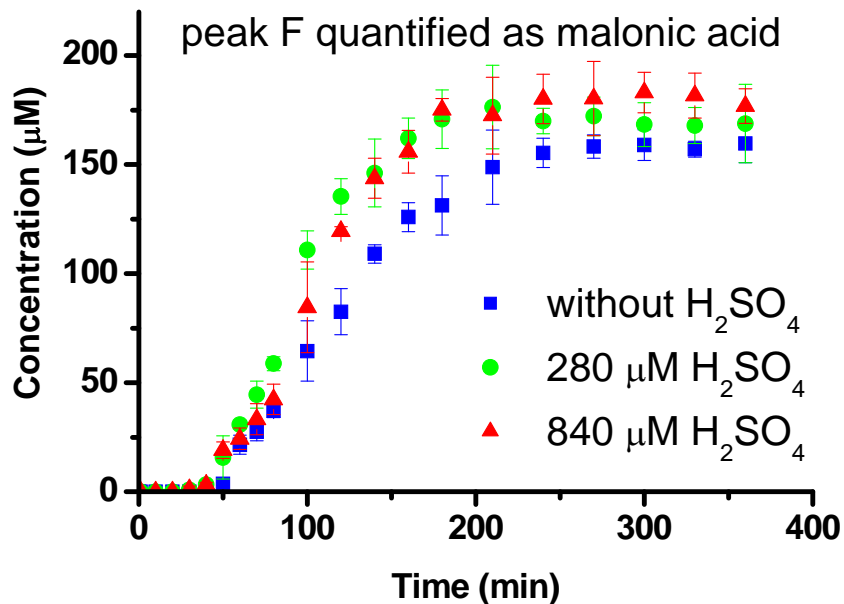
Higher-MW ions

Chemistry at Higher Concentrations—Methylglyoxal

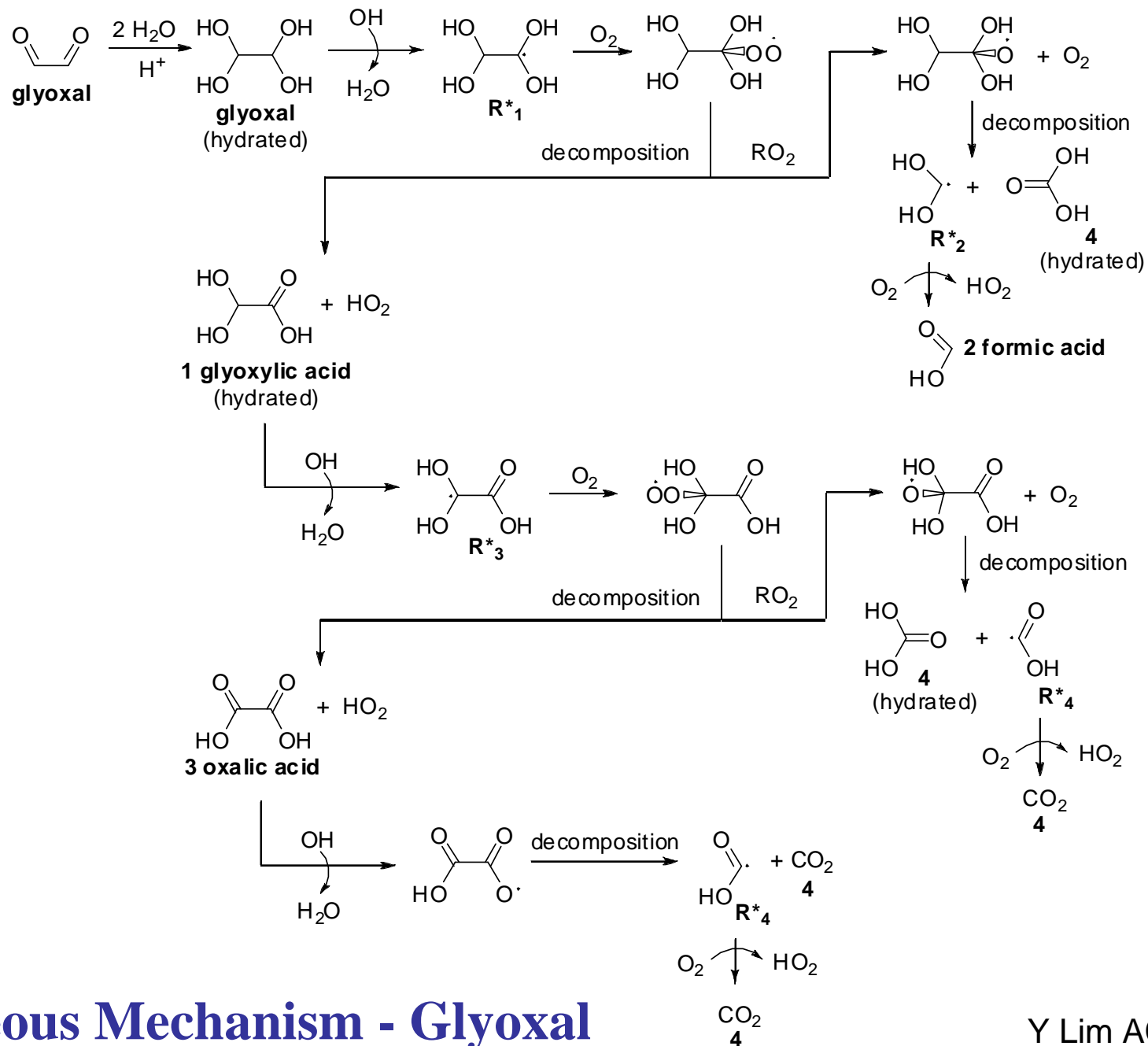


Larger acids are important products at higher concentrations.

Formation of higher C# products suggests radical-radical reactions

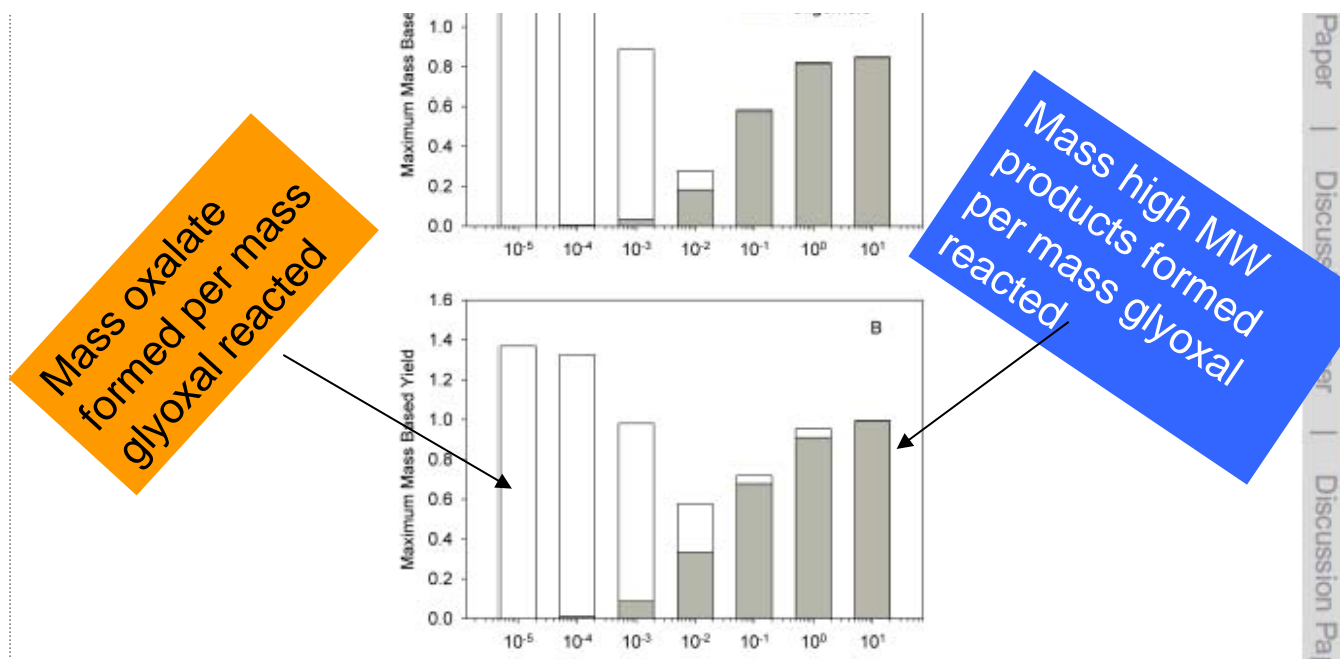


(Tan AE 2010)



Aqueous Mechanism - Glyoxal

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



Cloud \longleftrightarrow wet aerosol

Fig. 9. Predicted maximum mass based yields of oxalate (C₃+C₄ dimers) with increasing initial concentrations of glyoxal for aqueous-phase reactions with OH radicals: (A) for lab conditions (OH radical is generated by H₂O₂ photolysis; H₂O₂ also reacts with glyoxylic acid reducing yields; [H₂O₂]=5×[Glyoxal]_{initial}), and (B) for atmospheric conditions ([OH]_{aq} is constant; H₂O₂ is zero). For case A, [OH]_{aq} is (1–10)×10⁻¹² M. For case B, [OH]_{aq} is 2.8×10⁻¹² M. Simulated pH is 4.8–1.5 at low to high [Glyoxal]_{initial}.

Paper | Discussion Paper | Discussion Paper | Discussion Paper

Aqueous chemistry and its role in SOA formation

Y. B. Lim et al.

Title Page

Abstract Introduction

Conclusions References

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Interactive Discussion

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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

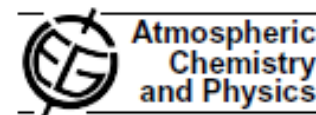
SOA formation from glyoxal increases with LWC

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

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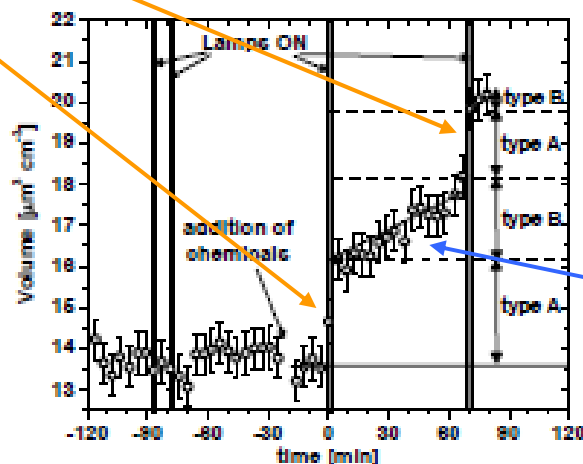
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R. Volkamer et al.: WSOC photochemistry of CHOCHO



Dark reaction

SOA through cloud processing now in CMAQ (yields)

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

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Mounting evidence suggests that low-volatility (particle-phase) organic compounds form in the atmosphere through aqueous phase reactions in clouds and aerosols. Although some have begun including secondary organic aerosol (SOA) in their models, cloud processing has not been included in this

Introduction

Despite the importance of atmospheric organic particulate matter (PM) to climate, air quality, and health, its sources and formation remain poorly understood (1,2). Most global and regional models fail to account for the PM is under-estimated in the troposphere. Organic carbon is not captured well by current estimates, and organic aerosol mass is underestimated for the troposphere. Organic carbon is estimated to contribute 0–50% of secondary

(Carlton EST 2008)
Improved model performance;
ICARTT

formation (6) and into cloud droplets, oxidize further, and create low-volatility compounds that remain, in part, in the particle phase upon droplet evaporation (> 90% of cloud droplets evaporate (7)). Cloud-production of SOA (SOA_{cl}) is a secondary PM formation process supported by most atmospheric and field evidence but currently missing from most atmospheric models. This missing pathway provides a plausible explanation for the recently noted failure of models to predict accurate vertical, spatial, and temporal OC profiles. Including (SOA_{cl}) in atmospheric models will add OC at multiple elevations with temporal and spatial variability. Results from a recent modeling study that included SOA_{cl} suggest that this process is atmospherically important (8). However, validating measurement comparisons are still needed. In this study, model OC predictions were evaluated using aircraft water-soluble OC concentrations from five flights (summarized in Table 1) and a month of OC concentrations from two ground-level air monitoring networks.

Cloud SOA: Plausibility and Current Understanding

FIGURE 2. Layer-averaged vertical profiles of OC and WSOC on August 14, 2004. Normalized mean bias for layer-average values for this flight was reduced from -65% to -15% when SOA_{cl} was included. Note: Dashed line and "○" indicates layer-averaged base CMAQ OC prediction. Solid line and "□" indicates CMAQ OC prediction with cloud-produced SOA included. WSOC observations, from the NOAA P3 flight are indicated with "▲". The x-axis is log scale.

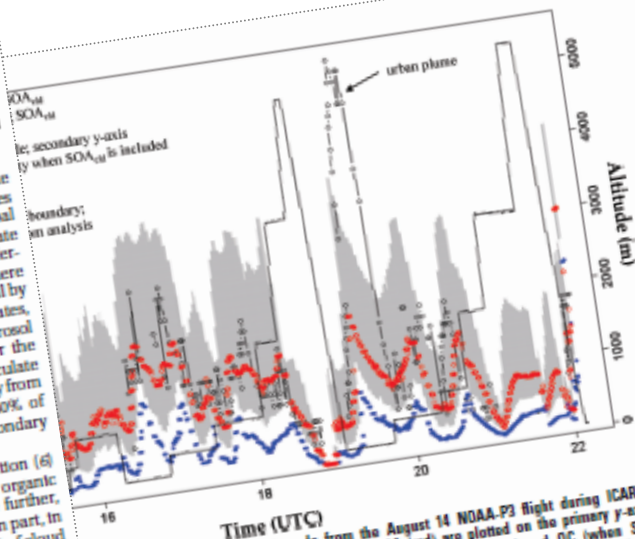


FIGURE 1. WSOC measurements (black) made from the August 14 NOAA-P3 flight during ICARTT. Base CMAQ OC prediction including cloud-produced SOA (red) are plotted on the primary y-axis; plane on the secondary y-axis. Note agreement between measured WSOC and OC (when SOA_{cl} is included). Gray area indicates uncertainty. The lower bound assumes a 2% mass yield (oxalic acid) and a 32% mass yield (oxalic acid and higher molecular weight compounds).

flight was specifically designed to investigate clouds, whereas other flights typically focused on urban or power plant plumes (Figure S-1, Supporting Information); in addition, this flight did not appear to be impacted by wild fires (Figure S-2, Supporting Information). The time series (Figure 1) and layer-averaged values (Figure 2) demonstrate that the base CMAQ model drastically underpredicts OC. Predictions that include SOA_{cl} show excellent agreement with WSOC measurements. Substantial enhancement of model performance is particularly noted aloft in the improved vertical OC profile (Figure 2). The normalized mean bias for layer-averaged OC predictions during the August 14 flight was reduced from -64% to -15% when SOA_{cl} was included.

At ~15 UTC (Figure 1), the NOAA P3 was flying within a cloud (RH measurements at ~100%); in addition, this flight model near the horizontal domain boundary. In addition, at this time, simulated concentrations near the horizontal domain boundaries were influenced by boundary conditions (which did not include SOA_{cl}) because there was inflow from outside the domain. Hence, at ~15 UTC, CMAQ predictions of OC with and without SOA_{cl} are excluded from the urban plume (strong covariance of CO and WSOC, Figure S-2, Supporting Information). CMAQ underpredicts OC in the plume even with SOA_{cl} included.

Note that model predictions in the surface layer (< 34 m) were also affected. Surface OC predictions were evaluated in urban areas with data from STN and in rural and

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

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

- 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 NO_x (Ervens GRL 2008)

Acknowledgements

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