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

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(Cooperative Agreement)

Improved Prediction of In-Cloud Biogenic SOA

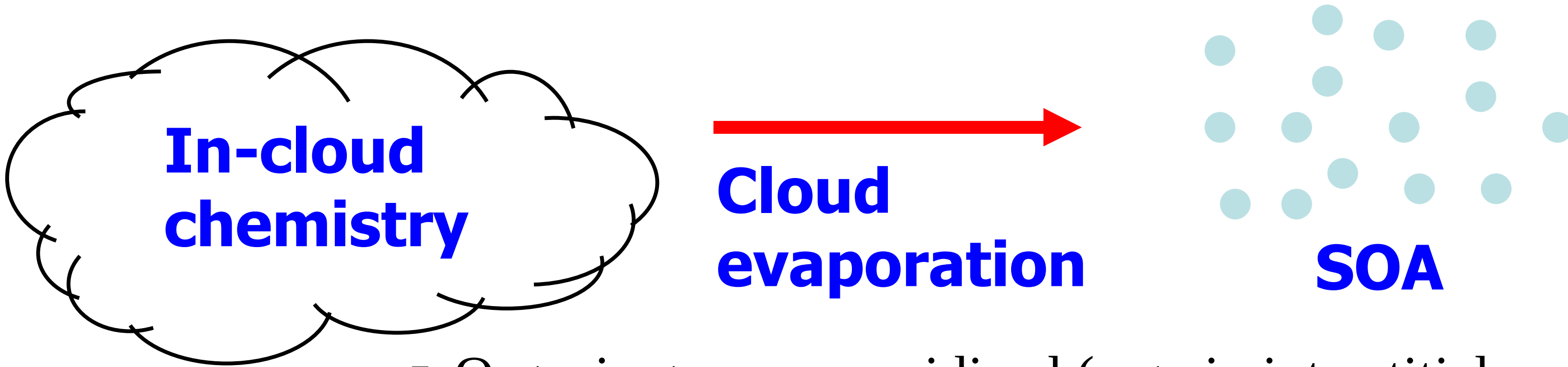
Overall Goal:

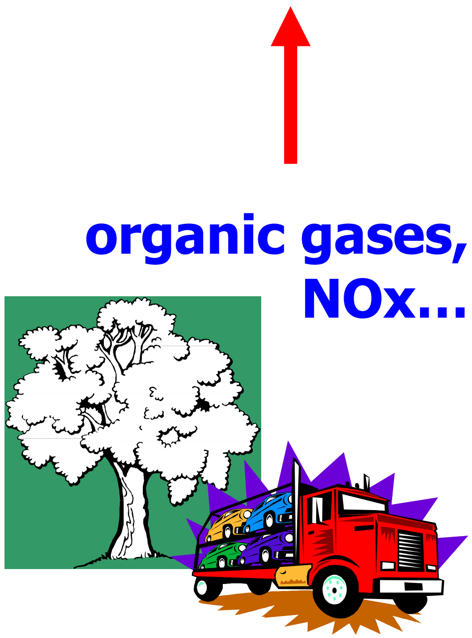
- Improve the simulation of secondary organic aerosol (SOA) formation through cloud processing

Approach:

- Conduct aqueous experiments ± HNO_3 (glyoxal/ methylglyoxal + OH) and at lower concentrations
- 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

In-Cloud SOA Formation





- Organic gases are oxidized (e.g., in interstitial spaces of clouds) to water-soluble compounds.
- Water-soluble gases partition into cloud droplets and oxidize further (e.g., by ·OH formed photochemically).
- Low volatility products remain in the particle phase upon cloud evaporation, contributing secondary organic aerosol (SOA), especially in FT

(Blando and Turpin, 2000; Gelencser and Varga, 2005)

In-Cloud SOA Formation – Is it an important process?

- Demonstrate feasiblity using available kinetics

  - Warneck, 2003; Ervens et al., 2004; Lim et al., 2005 – zero-dimensional, cloud chemistry, cloud parcel modeling
  - Chen et al. 2007 – chemical transport modeling

Aqueous phase products were assumed

- Look for atmospheric evidence

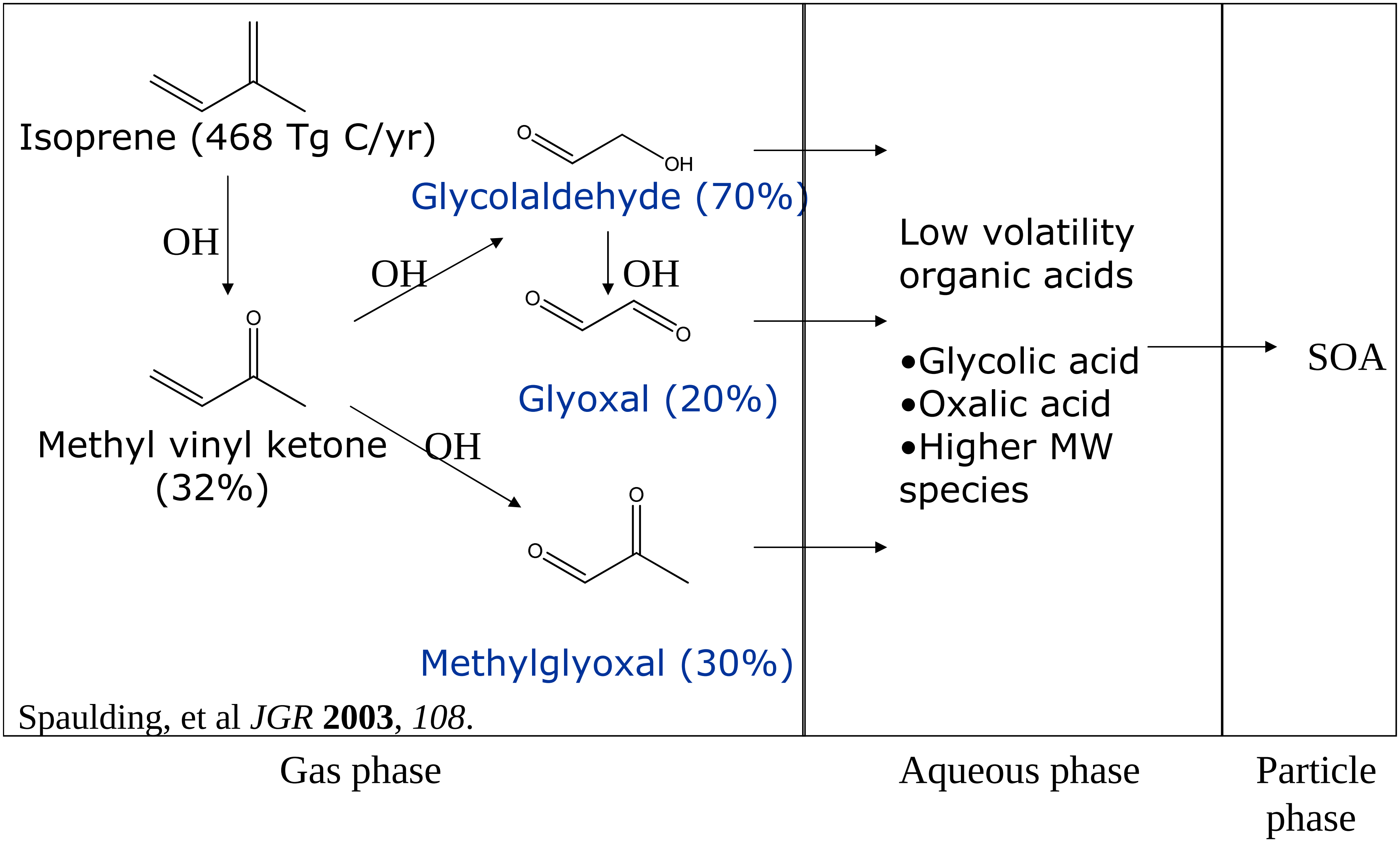
  - Sorooshian et al. 2007(MACE); 2006 (ICART); Heald et al., 2006 (ICART); 2005 (ACE-Asia); Yu et al., 2005; Crahan et al., 2004; Chebbi and Carlier, 1996; Kawamura et al., 1993

- Conduct key experiments

  - Carlton et al., 2006 (pyruvate→oxalate); Altieri et al., 2006 (pyruvate → oligomers); Carlton et al., 2007 (glyoxal→oxalate); Altieri et al., 2008 (methylglyoxal→oligomers by esterification)

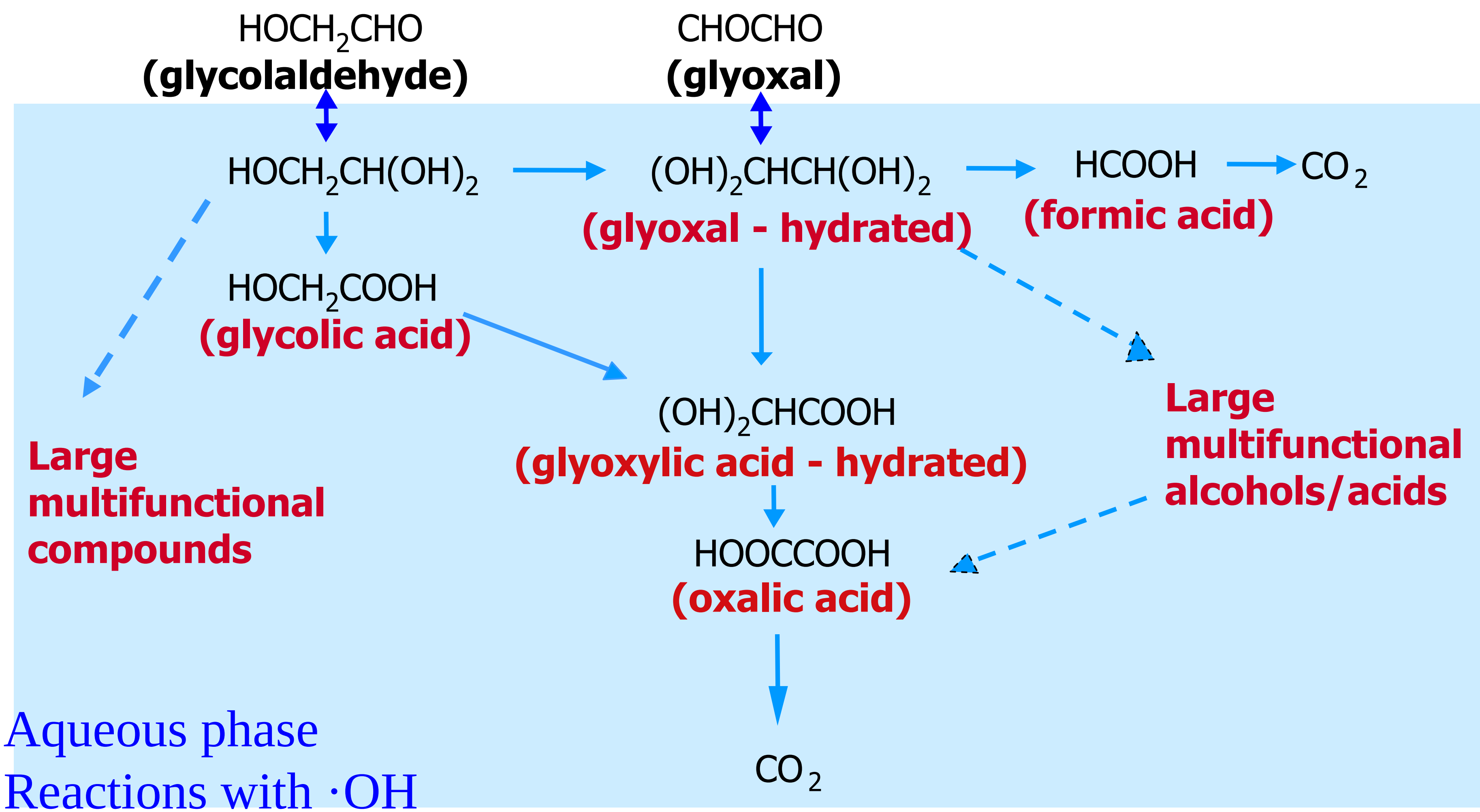
- Validate/refine kinetics and incorporate into chemical transport models

Isoprene to SOA



Spaulding, et al *JGR* **2003**, *108*.

Our Previous Experiments



(Carlton et al., 2007; Perri in prep.)

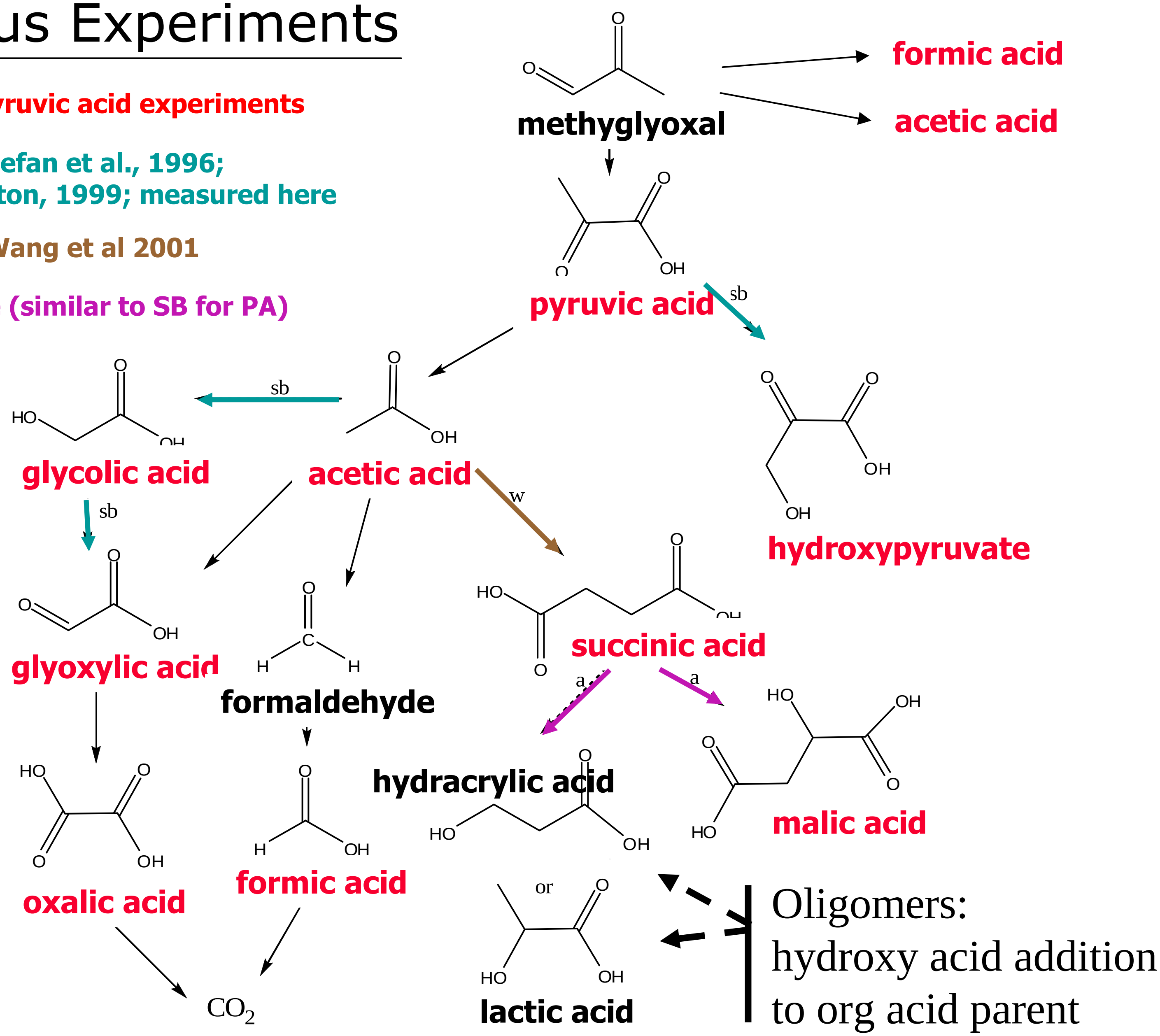
Our Previous Experiments

measured in pyruvic acid experiments

proposed by Stefan et al., 1996;
Stefan and Bolton, 1999; measured here

measured by Wang et al 2001

proposed here (similar to SB for PA)



(Altieri et al., 2008)

Our Previous Experiments

Oligomer Formation:

acid catalyzed esterification

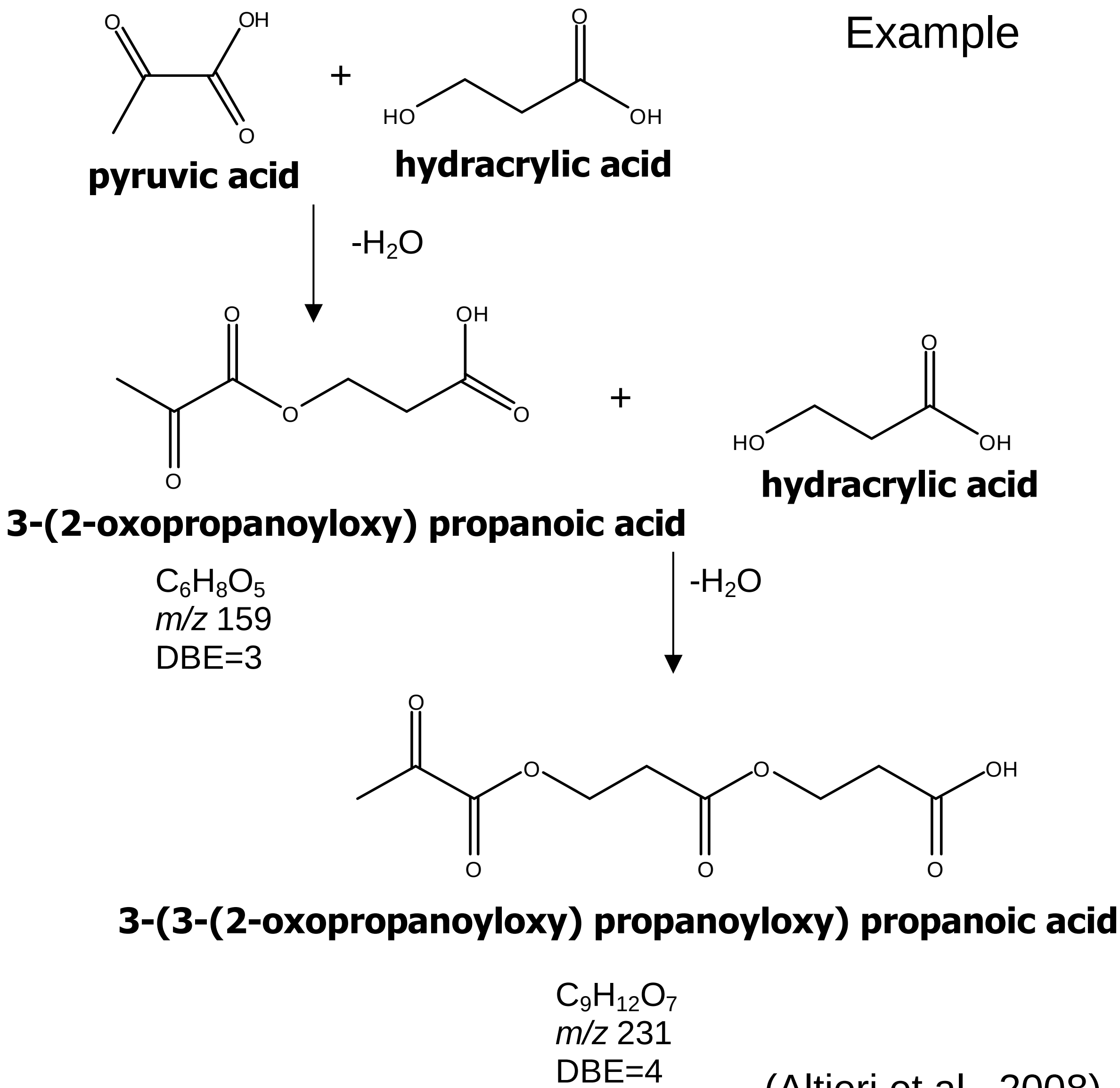
addition of a hydroxy acid ($C_3H_6O_3$) to each organic acid parent

(> MW by 72.0213 g/mol with each add'n; replicates series)

loss of water – lowers OM/OC

·OH involved in hydroxy acid formation

Example



(Altieri et al., 2008)

This Project

Roles of NOx in In-cloud SOA from Isoprene:

1. Gas phase formation of atmospheric oxidants
2. Gas phase formation of water soluble carbonyls
3. Aqueous $NO_3^- \rightarrow \cdot OH$, $\cdot NO_2$, organonitrates?, acid catalyzed reactions (?)

Project Experiments

Modeling

Batch Aqueous-Phase Reactions to Simulate Cloud Chemistry

Experiments

1 mM methylglyoxal

5 mM $H_2O_2 + h\nu \rightarrow \cdot OH$

4.2-4.5 pH

1mM methylglyoxal

5 mM $H_2O_2 + h\nu \rightarrow \cdot OH$

1.5 mM HNO_3

2.7-3.8 pH

Controls

MG+UV

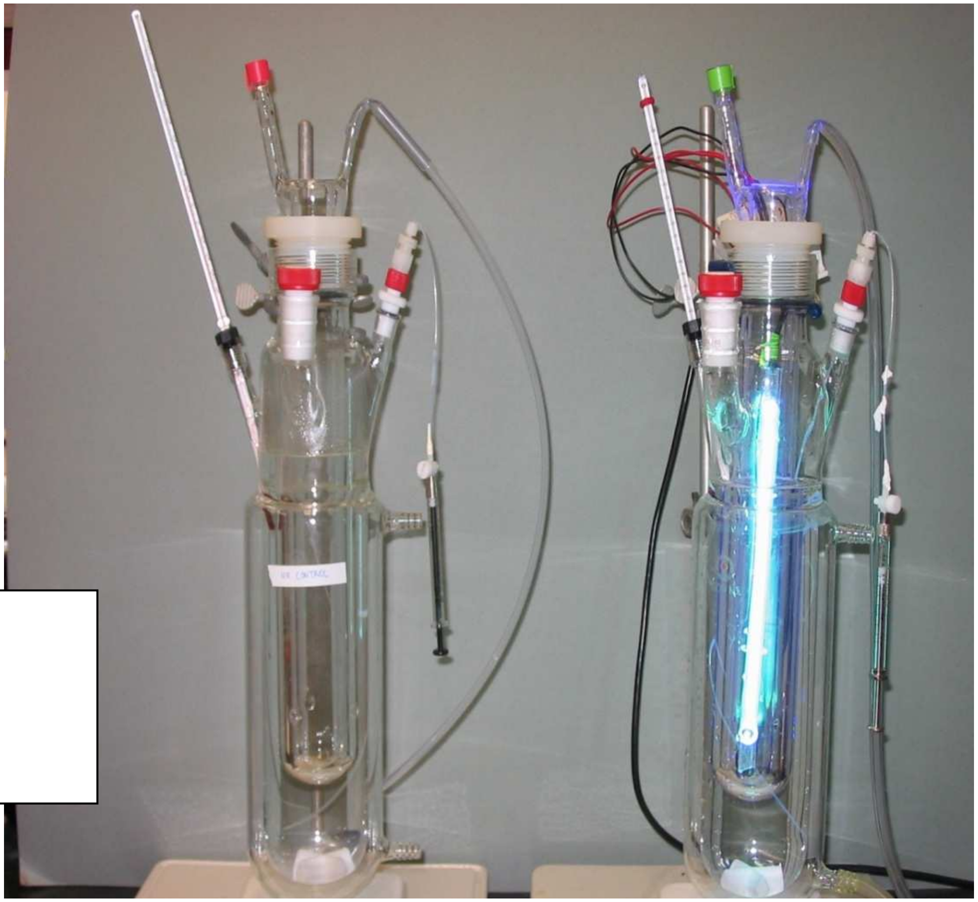
MG $+HNO_3$

$MG+H_2O_2$

$MG+H_2O_2 + HNO_3$

$UV+H_2O_2$

Repeat with glyoxal, and at lower concentrations



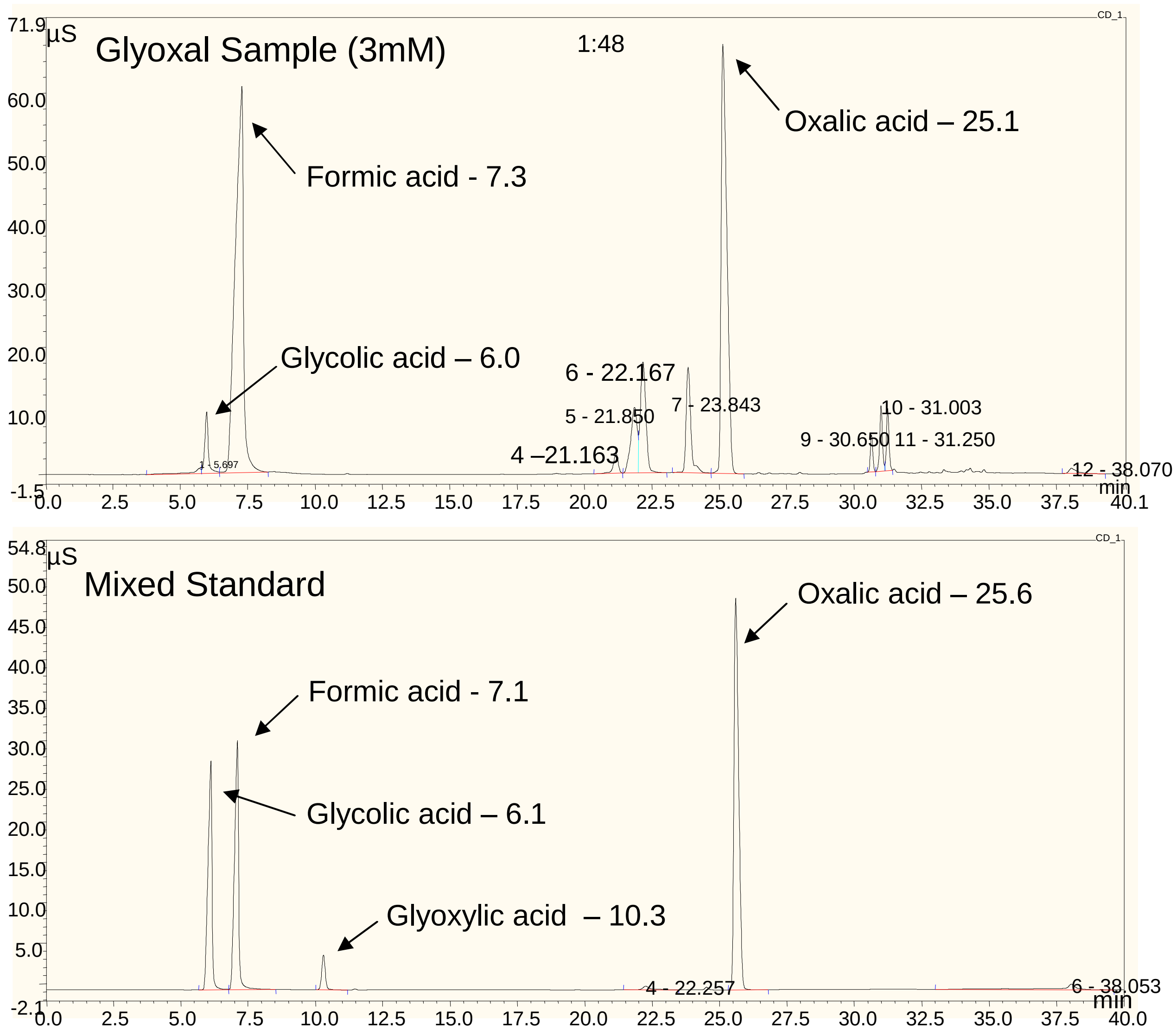
Catalase to stop reactions; Samples frozen
ESI-MS; FT-ICR MS; ESI-MS-MS,
IC for organic acids, DOC for mass balance, H_2O_2

Experimental progress: ICS-3000

ICS-3000 with conductivity and UV/vis; IonPac AS11-HC column

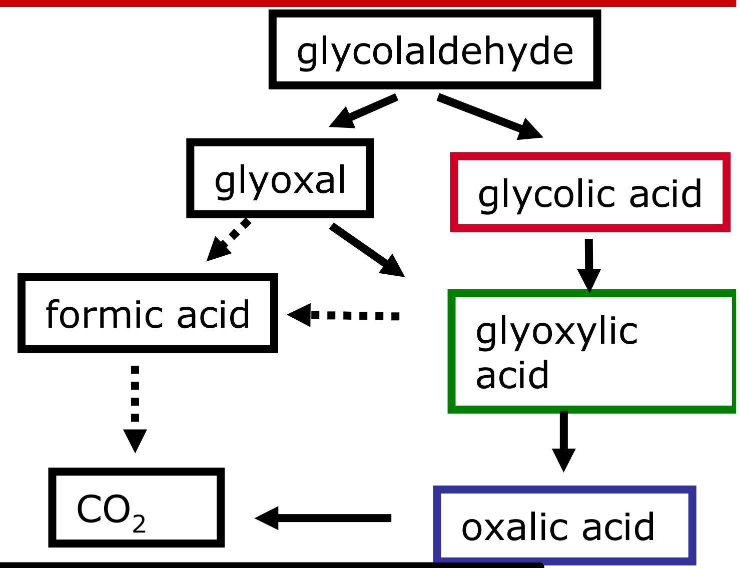
Now:
3 mM, 300 µM, 30 µM Glyoxal

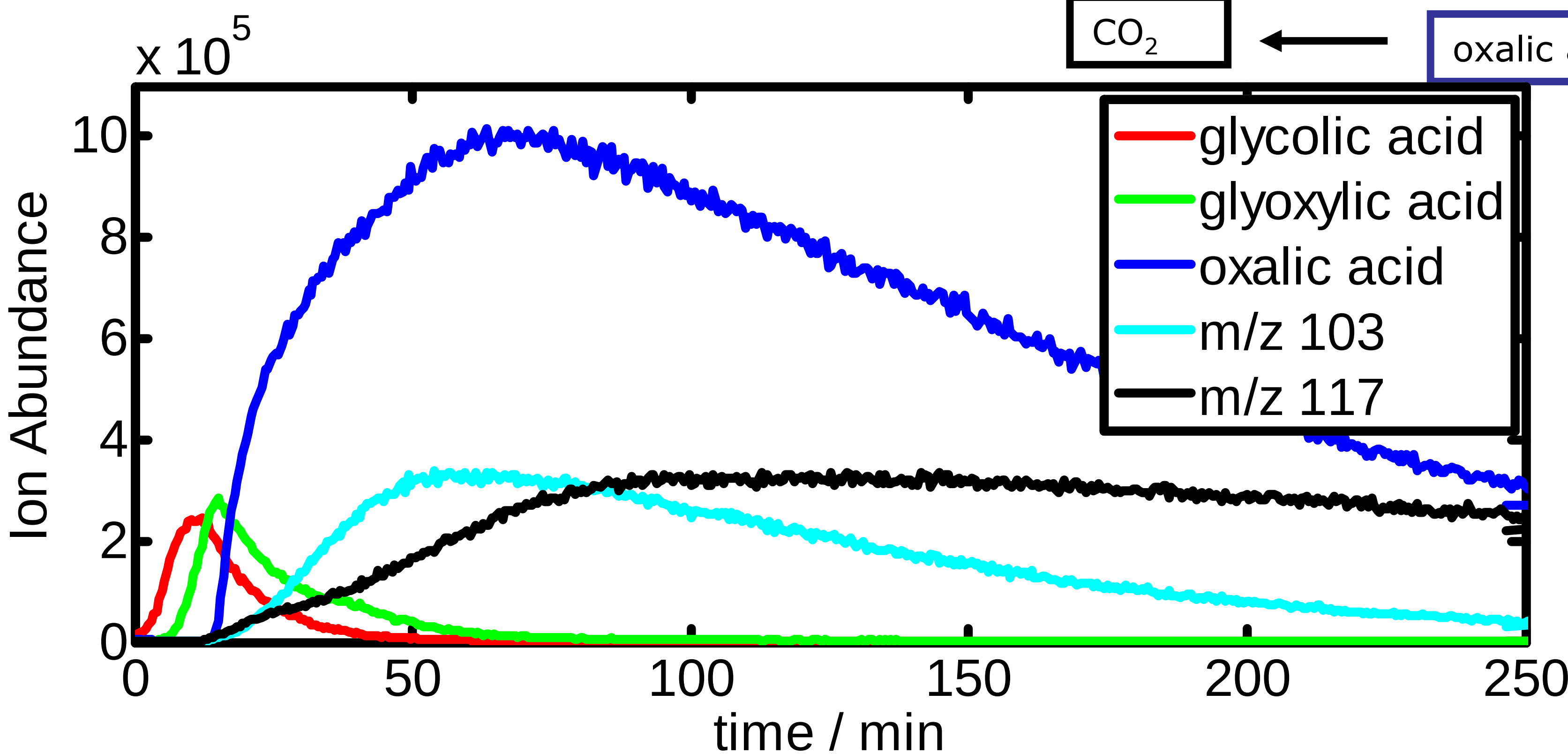
Atmospheric aqueous glyoxal concentrations
5 – 300 µM



Experimental progress: On-line ESI-MS Measurements

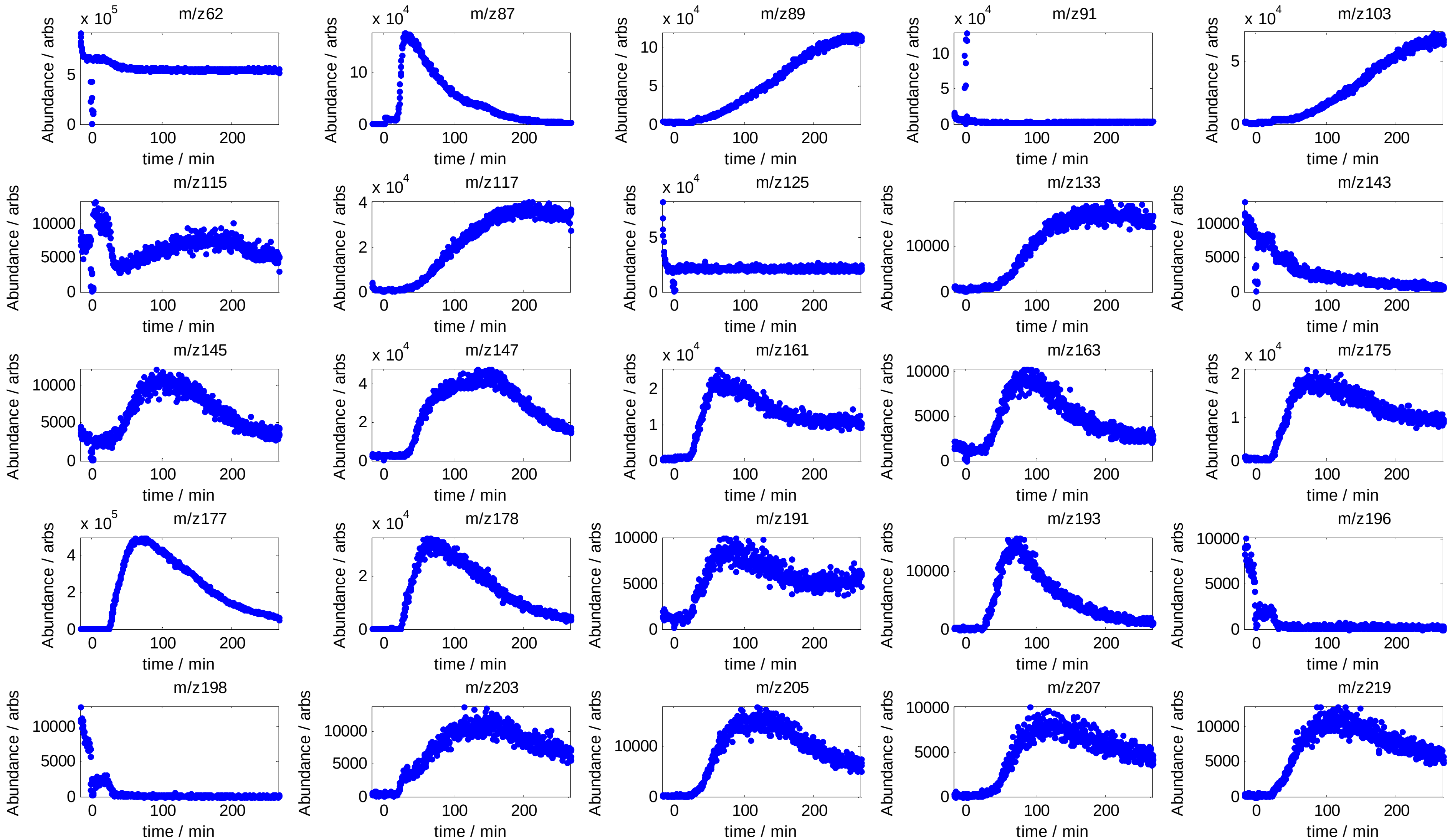
m/z 103, 117 are two of the many unpredicted products





Methylglyoxal + ·OH + NO_3^-

Monitor the ion abundance of each m/z over time



Modeling Strategy

Aqueous Photooxidation Experiments

Measure products in reaction vessel

↓

Predict concentrations of key products in the reaction vessel

↓

Cloud models

Incorporate chemistry into cloud chemistry/ cloud chemistry/ parcel models to develop yields or to simplify the chemistry

Form/evaporate droplets from reaction vessel samples to measure yields

SOA yields from wso precursor

Product yields from wso precursor

Simplified aqueous chem

CMAQ

Incorporate in-cloud SOA formation using a yield-based approach

Incorporate in-cloud SOA formation using simplified chemistry

Yields: Key variables

product yields:

•Cloud contact time, VOC/NOx, LWC

Partitioning:

• RH, T

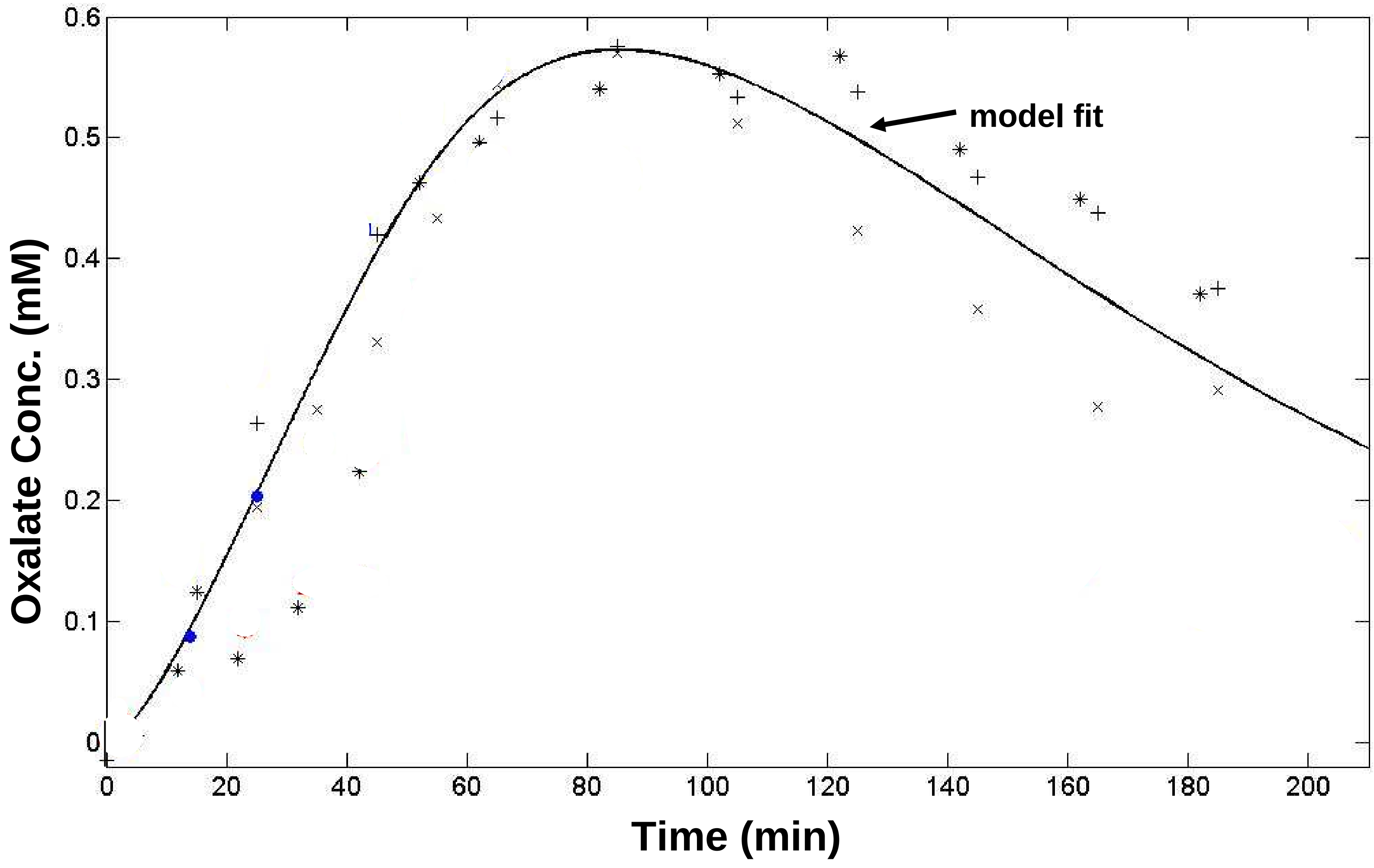
Modeling Collaborators:

Annmarie Carlton (NOAA/EPA Cooperative Agreement)

Barbara Ervens, Sonia Kriedenweis, Graham Feingold, UCBoulder/NOAA

Example of modeling strategy – Prediction of oxalic acid from glyoxal

3 mM Glyoxal + ·OH (15 mM H_2O_2 + UV)

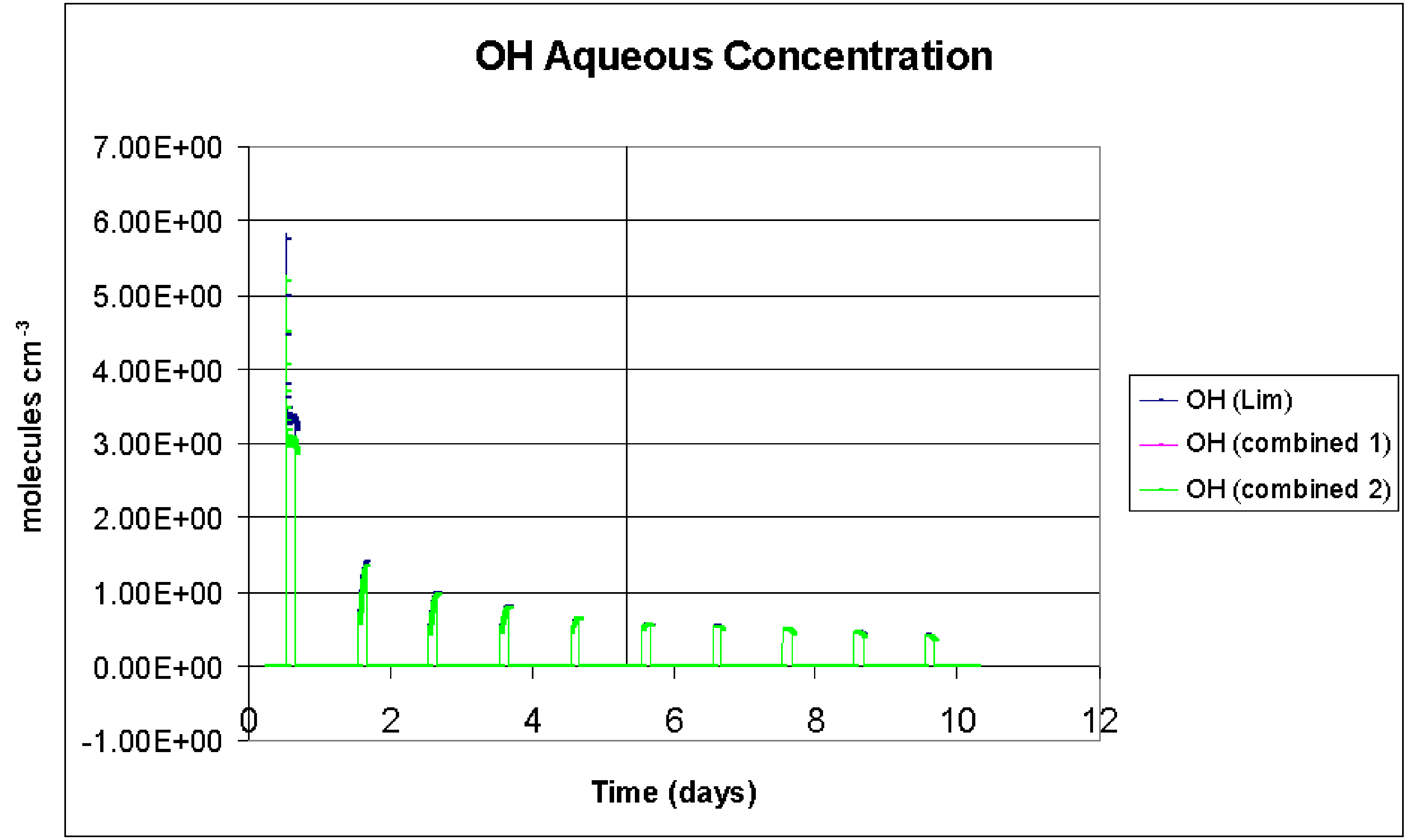


(model of Carlton et al., 2007; modified, now captures pH change)

Example: Simulating oxalic acid from isoprene for Amazon: Previous (Lim et al, 2005) and updated glyoxal

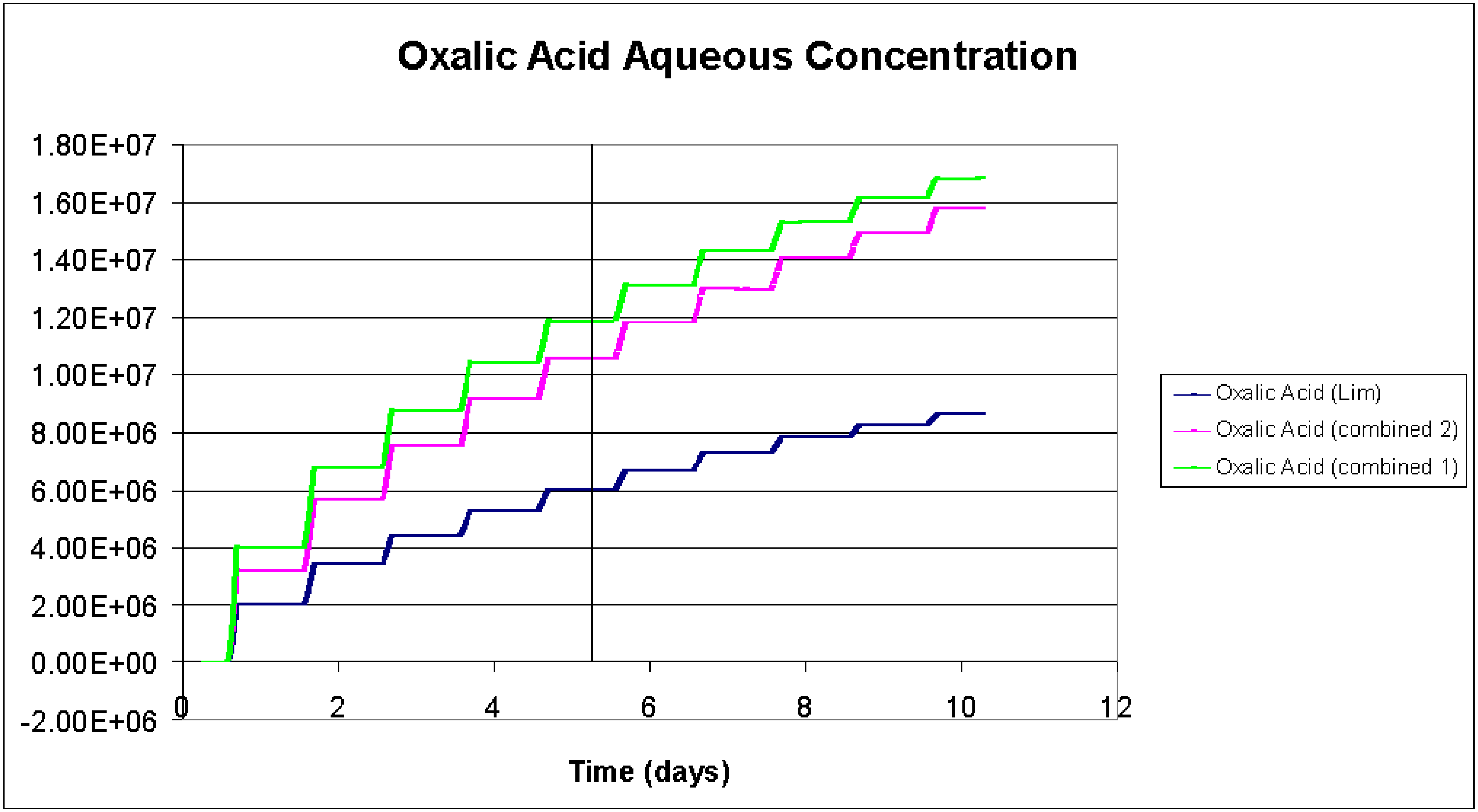
- 5 days in equatorial Amazon; 5 days in marine area
- Intermittent clouds between 13:00–16:00 daily
- Fair weather cumulus, 1 km, LWC=0.5 g/m^3, T=285K, pH=4.5
- Semi-sinusoidal change of photolysis between 06:00-18:00 with a peak at noon and no nighttime photolysis
- 1-Box model (gas- and aqueous-phase chemistry, phase transfer, emission, dry deposition)
- Over 300 reactions: HO_x-NO_y-CO-CH_4-Isoprene-S-Metal-Cl-Organics
- Model predicts aqueous phase organic acids

Model improvements did not effect ·OH predictions



NOTE: about 2/3rds of ·OH is from gas phase. (Aqueous ·OH formation is often neglected in cloud chemistry models)

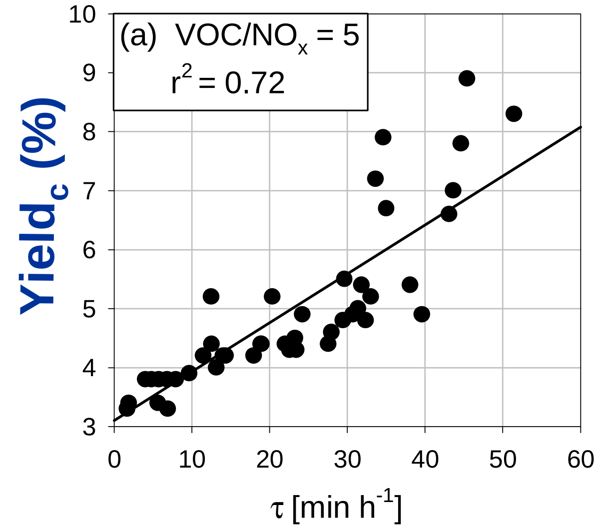
Model improvements approx. doubled oxalic acid

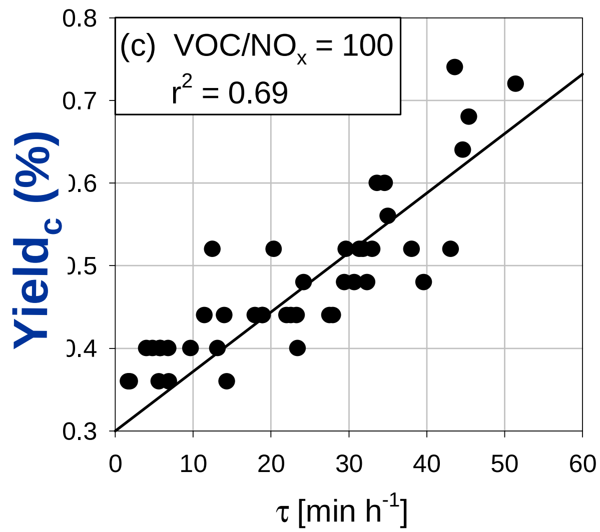


Note: Still must incorporate refinements for methylglyoxal, glycolaldehyde including prediction of large multifunctional or oligomeric products.
Note glycolic acid is also an important contributor to in-cloud SOA.

Cloud parcel model of in-cloud SOA from isoprene

Cloud contact time

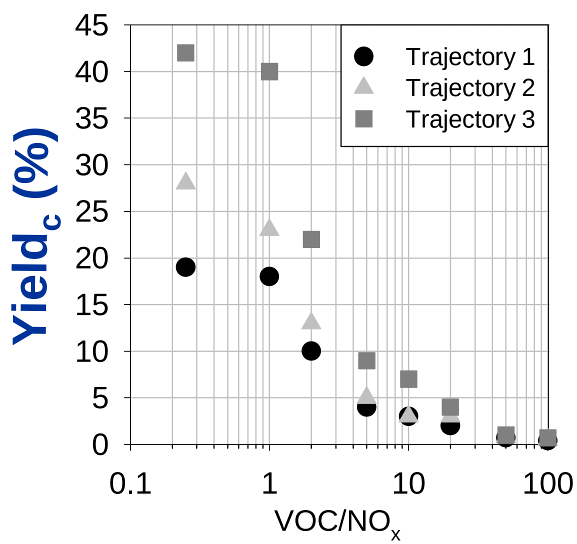




(Ervens et al., 2008)

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

VOC/NOx



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

Feingold microphys. cloud model

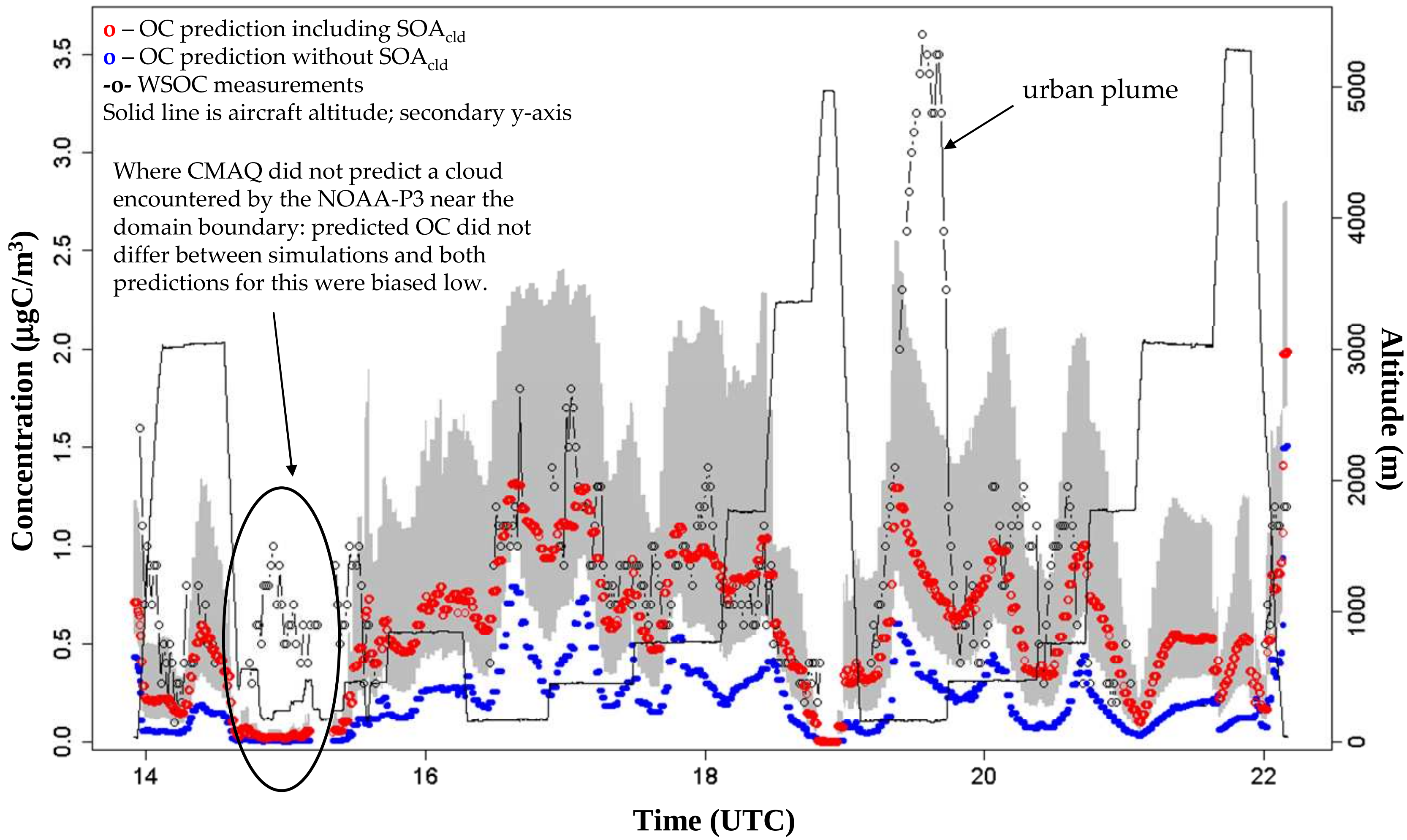
- multiple cycles
- stratocumulus
- partitioning of wsoc
- gas+aq chem
- Ervens aq chem
- altered Gly, PA chem

CMAQ with fixed yields from aqueous-phase aldehydes

ICART – Aug 14th – "cloud flight"

Yields – 4% molar (SOA from glyoxal, methylglyoxal, 10 min cld contact time)

Range of yields – 1-10%

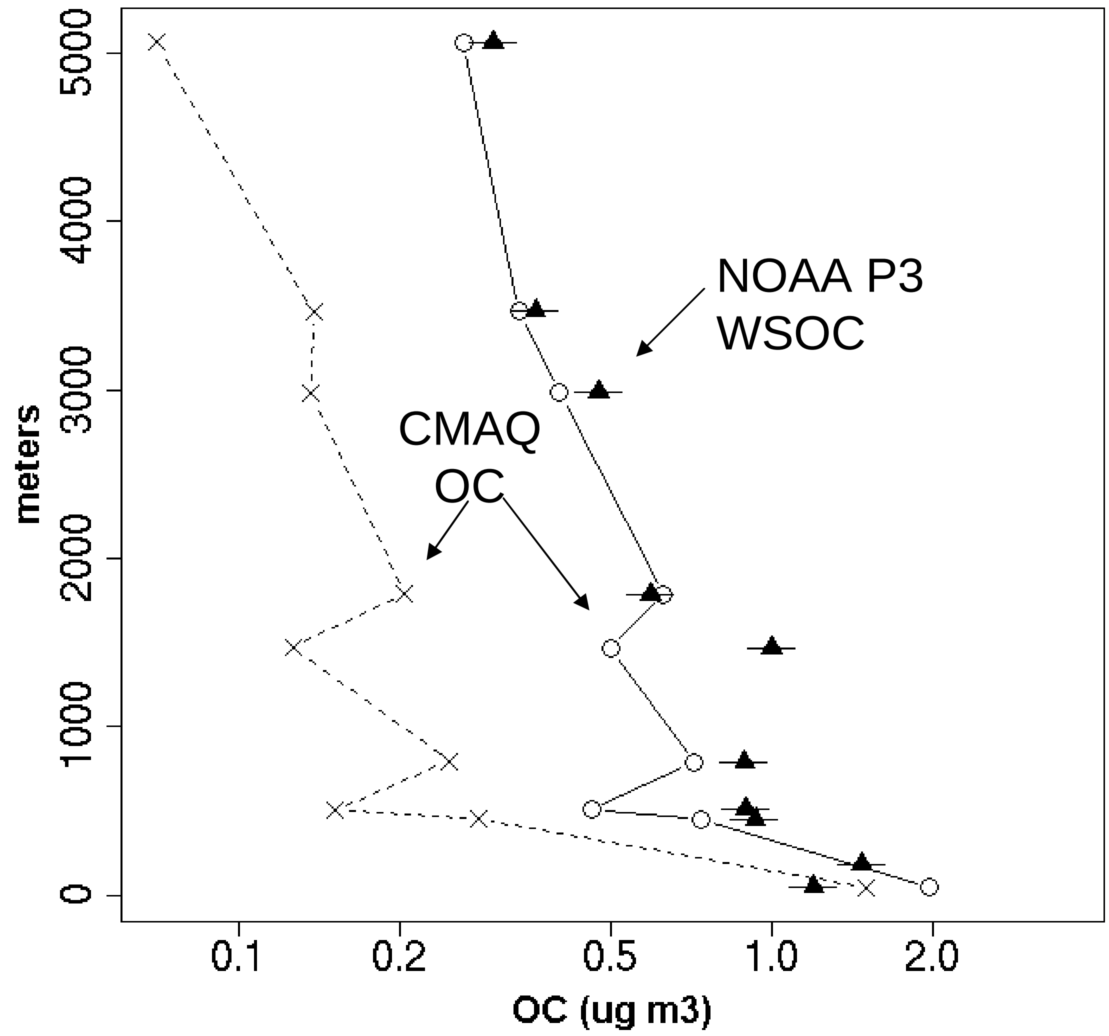


CMAQ with fixed yields from aqueous-phase aldehydes

Layer-avg conc.
Aug 14, 2004
“cloud exp”

(simulations Aug 1-31)

In-cloud SOA ranged from 0-5 μg/m³



Next Steps

1. Experiments at lower precursor concentrations
2. Experiments with/without HNO_3
3. Model methylglyoxal in reaction vessel
4. CMAQ Rosenbrock solver - for more detailed aq. Chemistry

Acknowledgements:

Rutgers:

Sybil Seitzinger (Co-I), Katye Altieri, Mark Perri, Yi Tan, Mary Moore

NOAA/EPA:

Annmarie Carlton, Rohit Mathur, Shawn Roselle, Atmospheric Sciences Modeling Division

Other Collaborators:

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