

US EPA ARCHIVE DOCUMENT



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

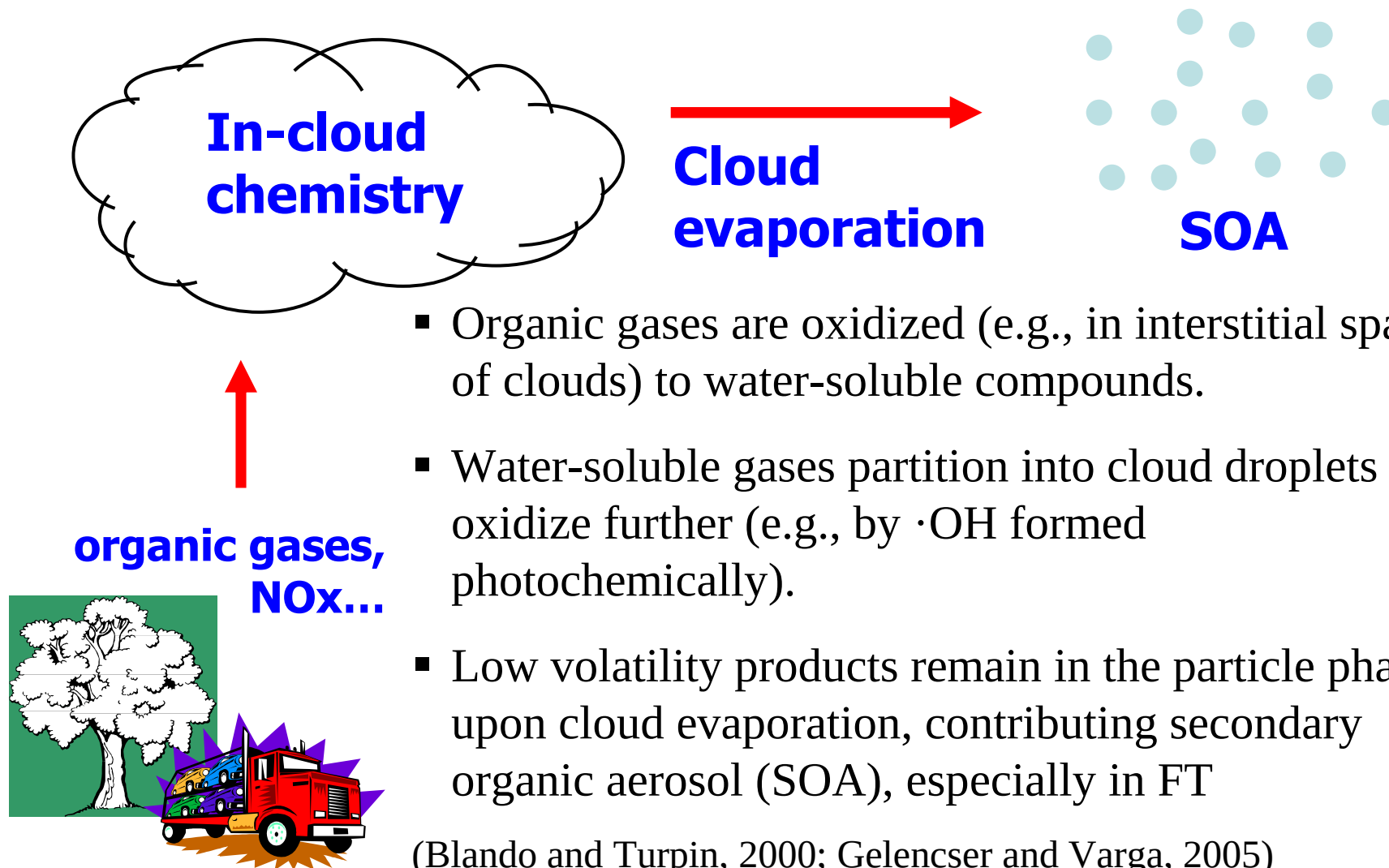
Overall Goal:

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

Approach:

- Conduct aqueous experiments $\pm$ 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



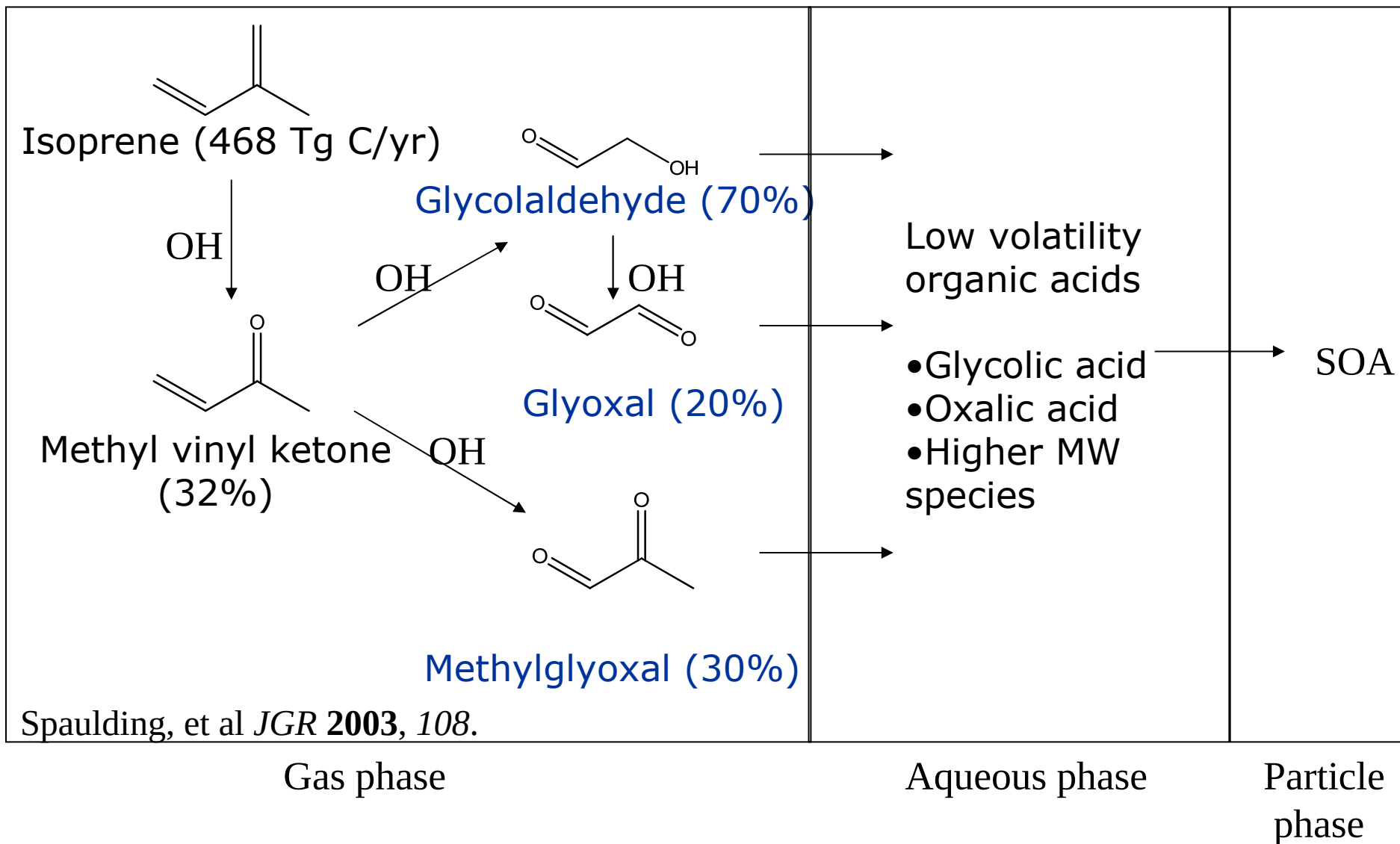
(Blando and Turpin, 2000; Gelencser and Varga, 2005)

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

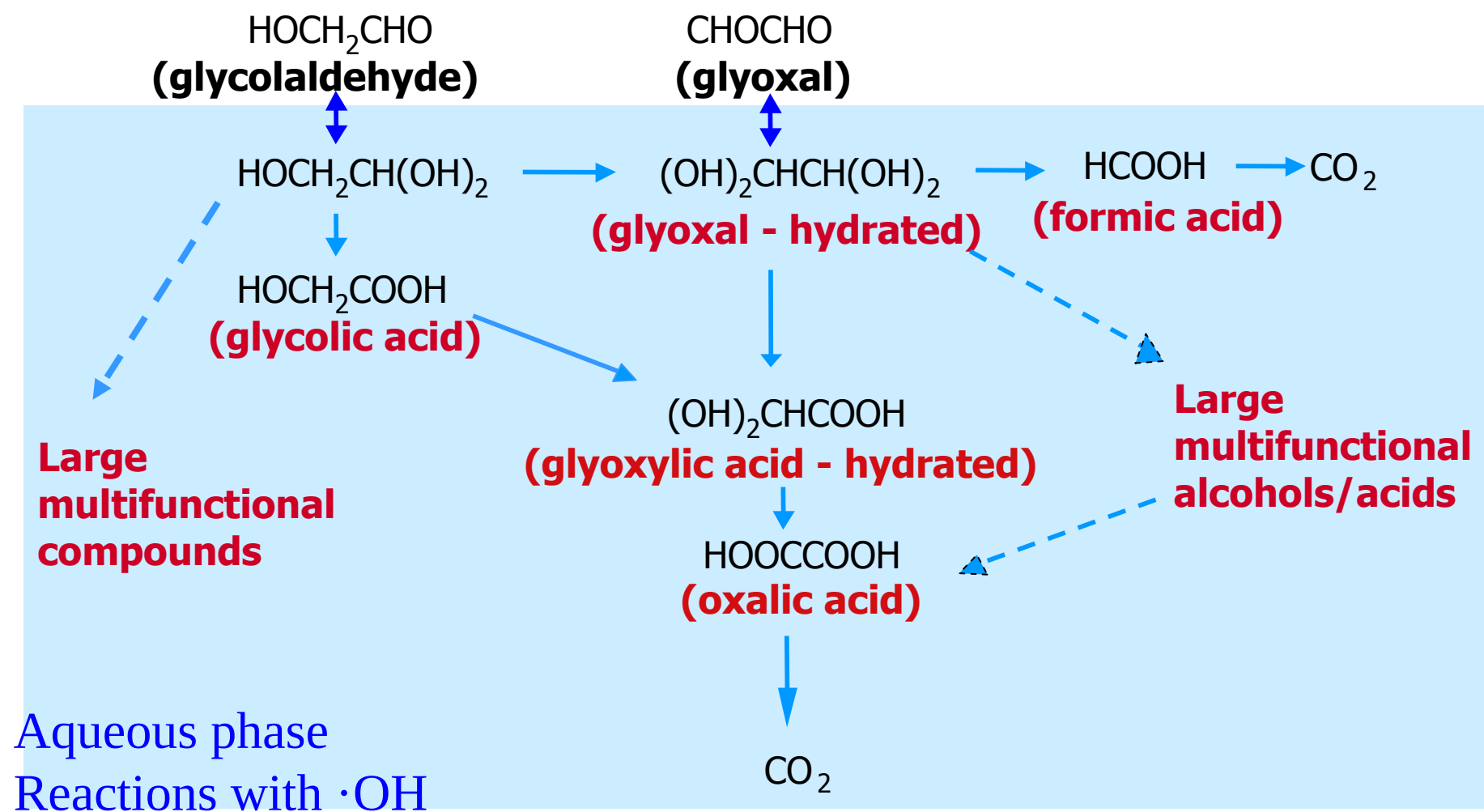
- Demonstrate feasibility using available kinetics
 - Warneck, 2003; Ervens et al., 2004; Lim et al., 2005 – zero-dimensional, cloud chemistry, cloud parcel modeling
 - Chen et al. 2007 – chemical transport modeling
- Look for atmospheric evidence
 - Sorooshian et al. 2007(MACE); 2006 (ICART); Heald 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

Aqueous phase products
were assumed

Isoprene to SOA

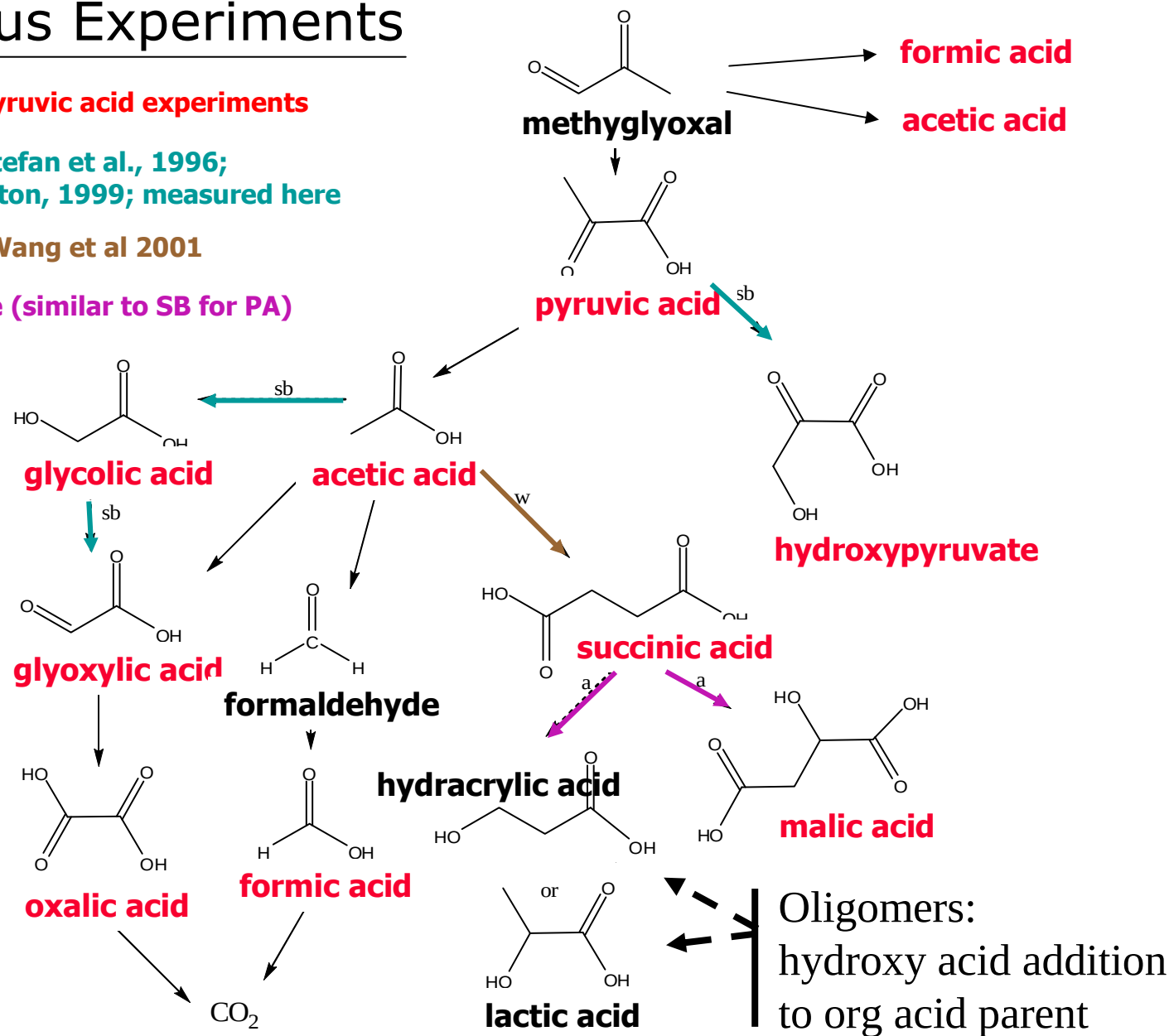


Our Previous Experiments



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

- 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:

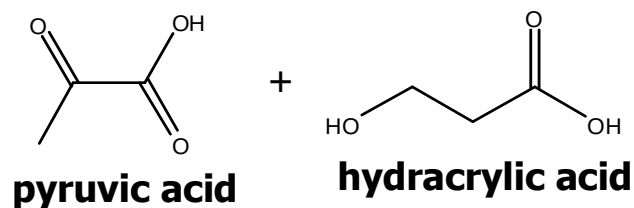
acid catalyzed
esterification

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

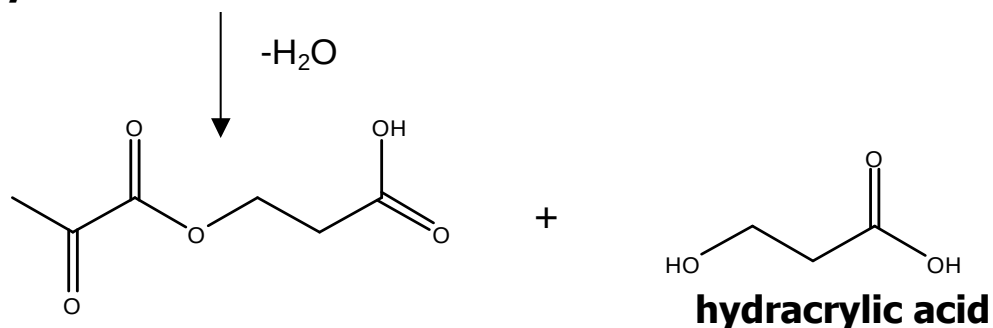
(> MW by 72.0213 g/mol
with each add'n;
replicates series)

loss of water – lowers
OM/OC

·OH involved in hydroxy
acid formation

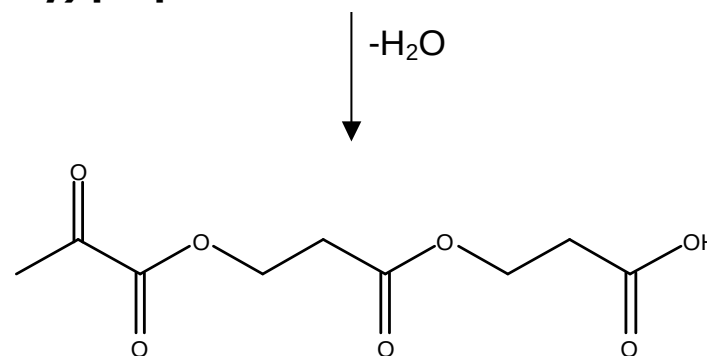


Example



3-(2-oxopropanoyloxy) propanoic acid

$C_6H_8O_5$
 m/z 159
DBE=3



3-(3-(2-oxopropanoyloxy) propanoyloxy) propanoic acid

$C_9H_{12}O_7$
 m/z 231
DBE=4

(Altieri et al., 2008)

This Project

Roles of NO_x in In-cloud SOA from Isoprene:

1. Gas phase formation of atmospheric oxidants
2. Gas phase formation of water soluble carbonyls
3. Aqueous $\text{NO}_3^- \rightarrow \cdot\text{OH}, \cdot\text{NO}_2$, organonitrates?, acid catalyzed reactions (?)

Modeling

Project Experiments

Batch Aqueous-Phase Reactions to Simulate Cloud Chemistry

Experiments

1 mM methylglyoxal

5 mM $\text{H}_2\text{O}_2 + h\nu \rightarrow \cdot\text{OH}$

4.2-4.5 pH

1mM methylglyoxal

5 mM $\text{H}_2\text{O}_2 + h\nu \rightarrow \cdot\text{OH}$

1.5 mM HNO_3

2.7-3.8 pH

Controls

MG+UV

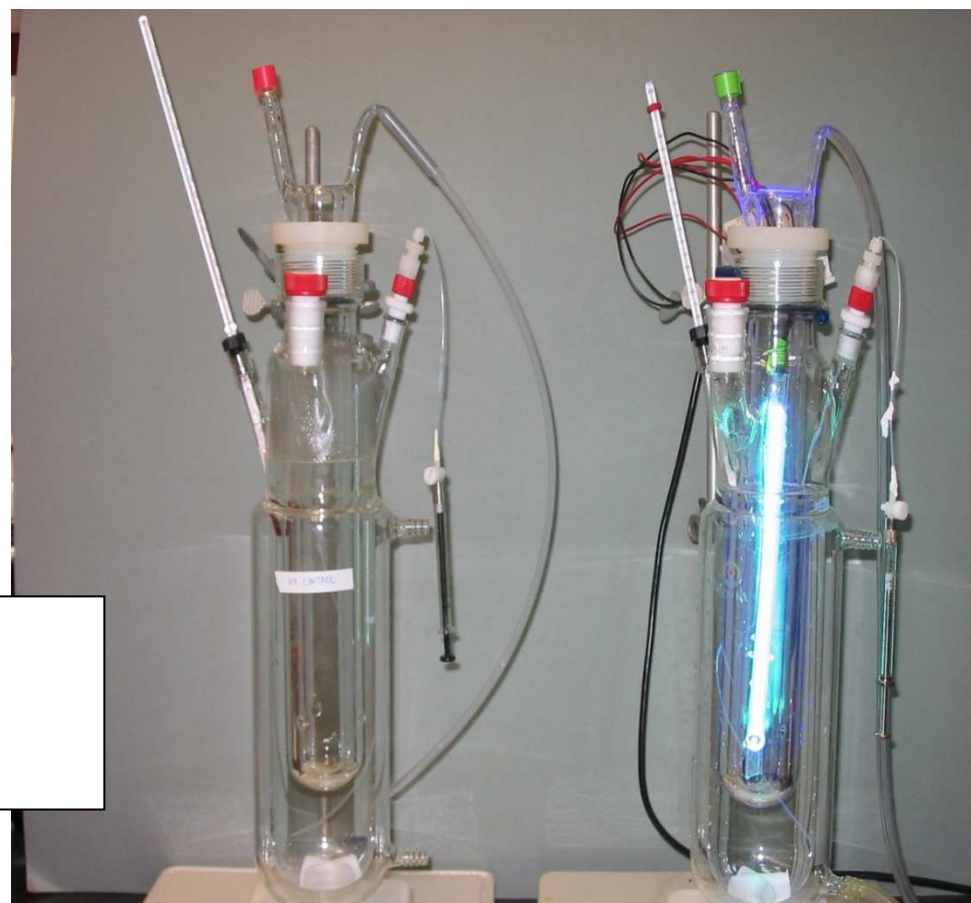
MG + HNO_3

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

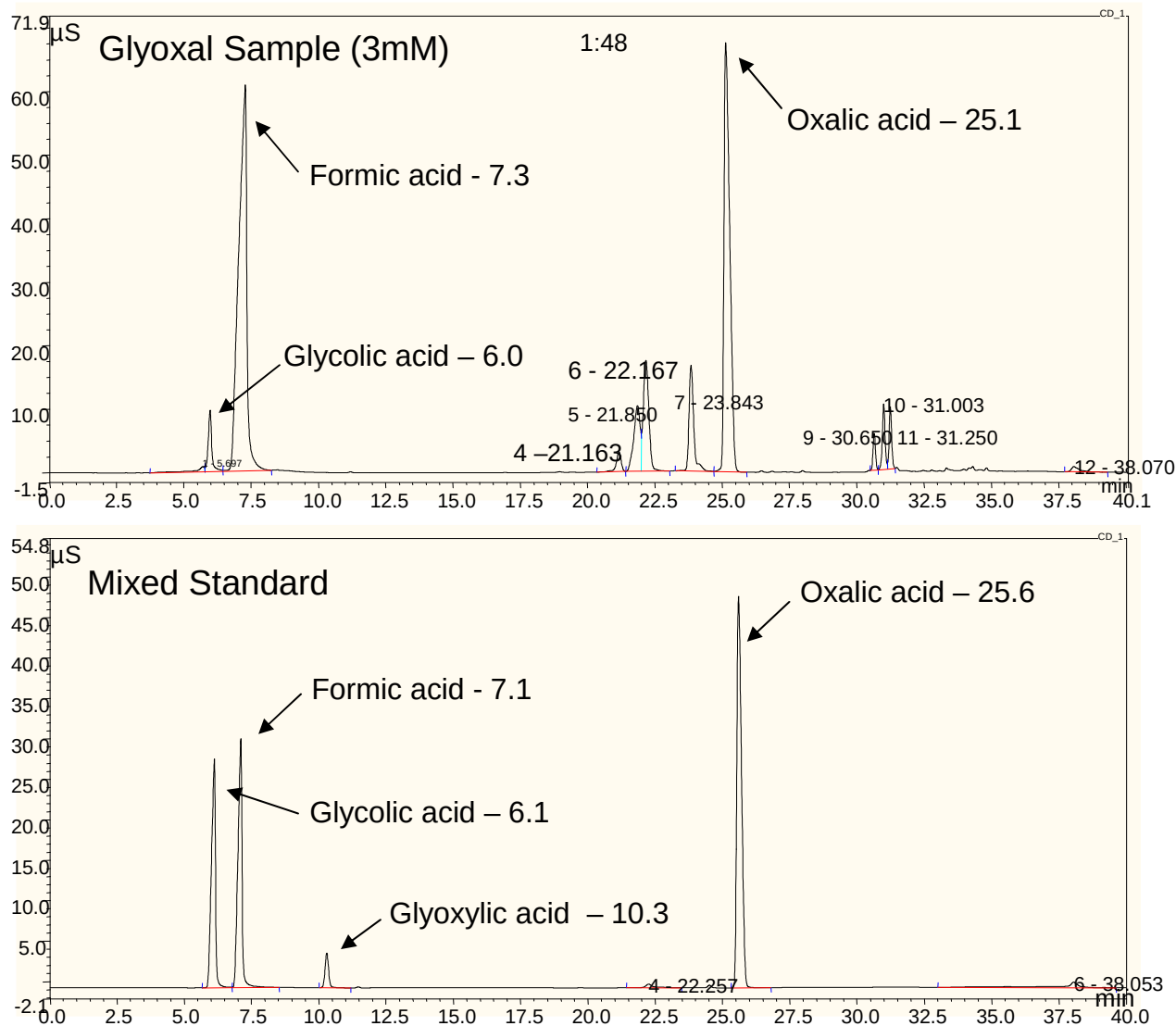
Experimental progress: ICS-3000

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

Now:

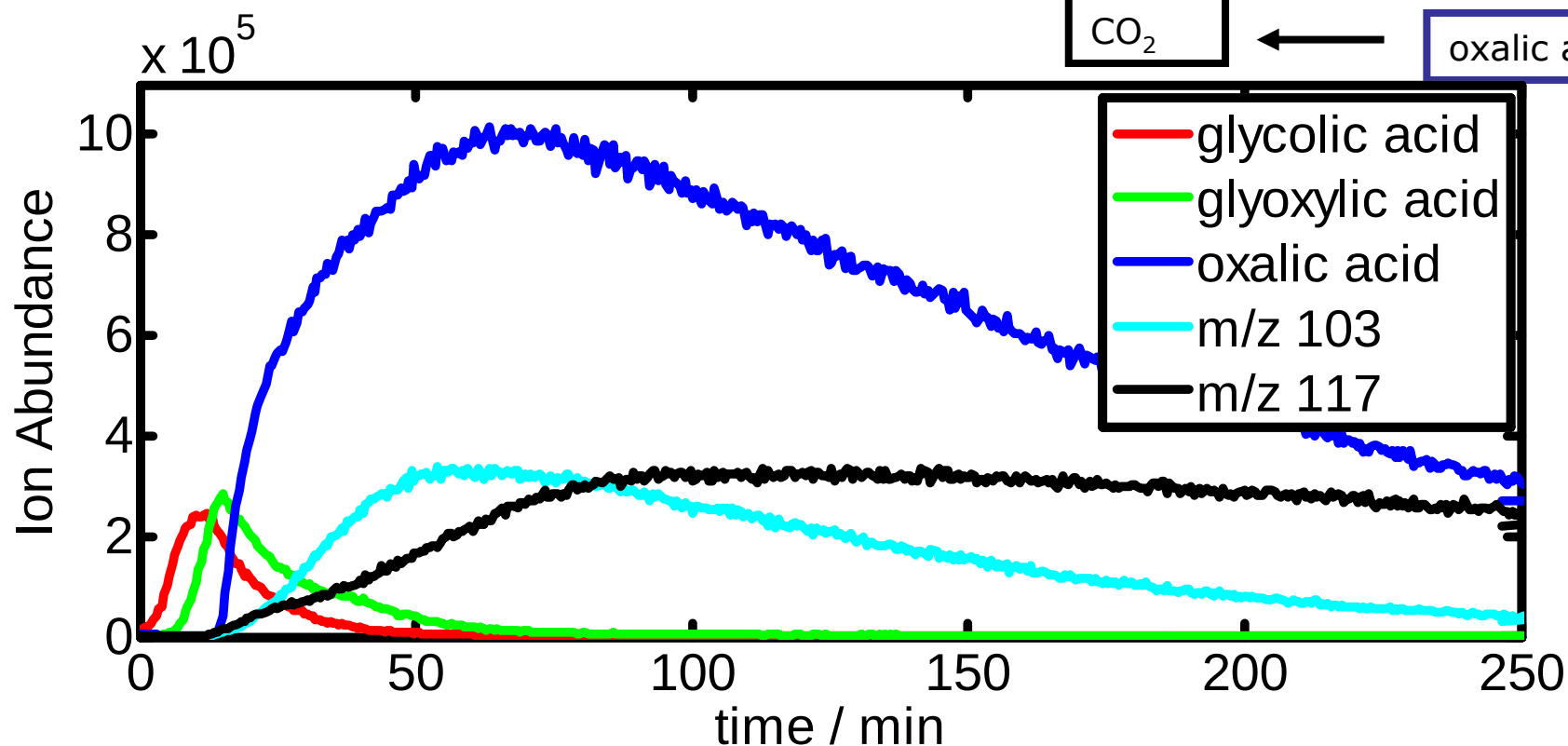
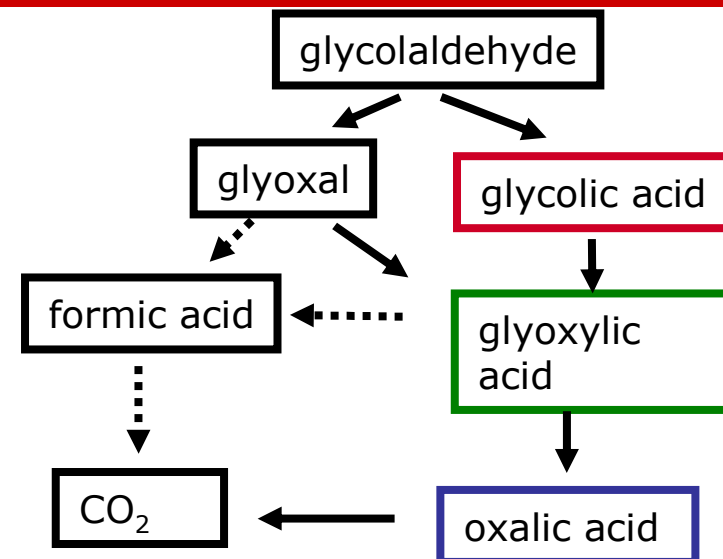
3 mM, 300 μ M,
30 μ M Glyoxal

Atmospheric
aqueous glyoxal
concentrations
5 – 300 μ M



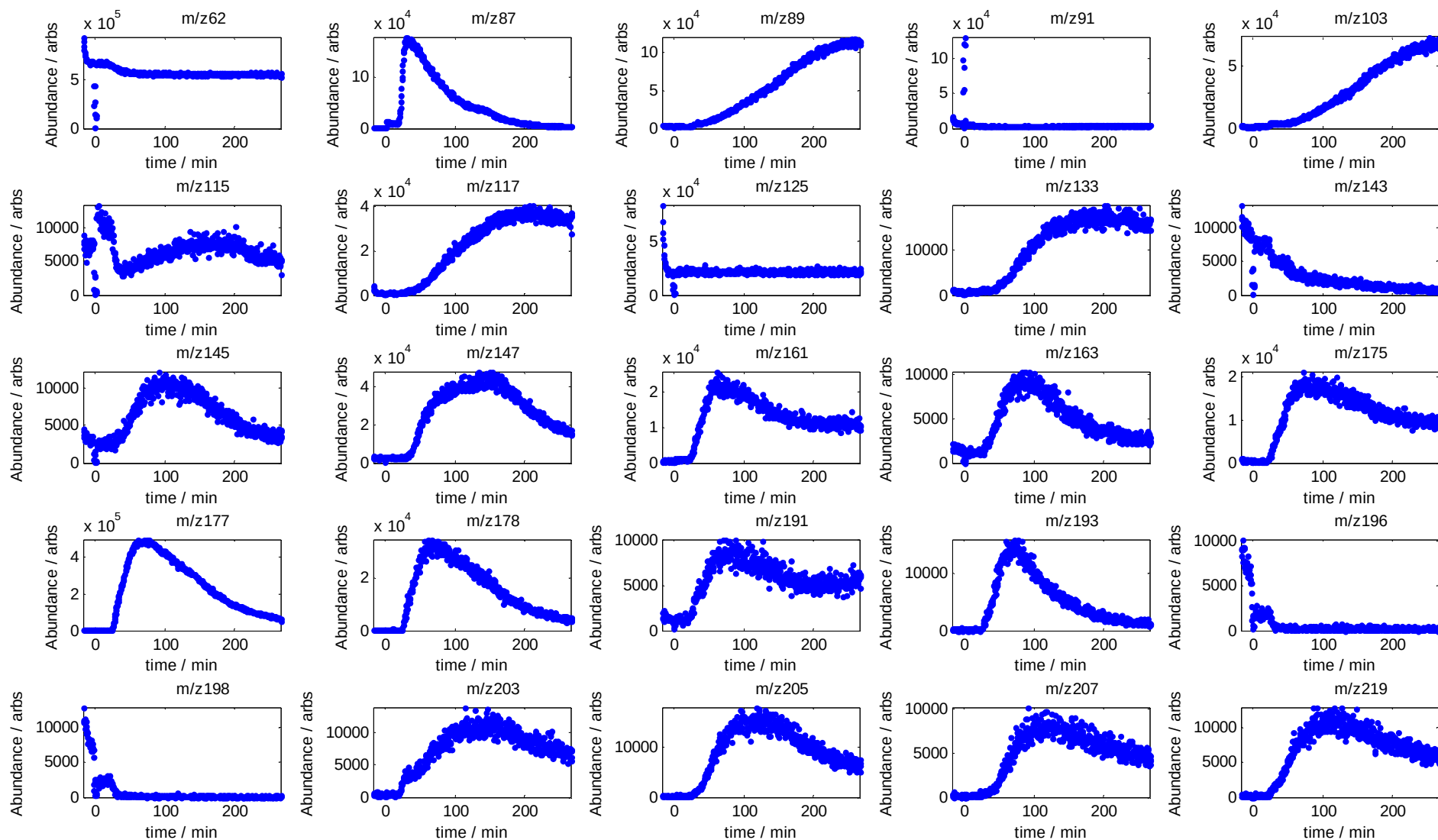
Experimental progress: On-line ESI-MS Measurements

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



Methylglyoxal + $\cdot\text{OH}$ + 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



Incorporate
chemistry into
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

Yields: Key variables

product yields:

- Cloud contact time,
VOC/NO_x, LWC

Partitioning:

- RH, T

CMAQ

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

Incorporate in-cloud SOA
formation using simplified
chemistry

Cloud models

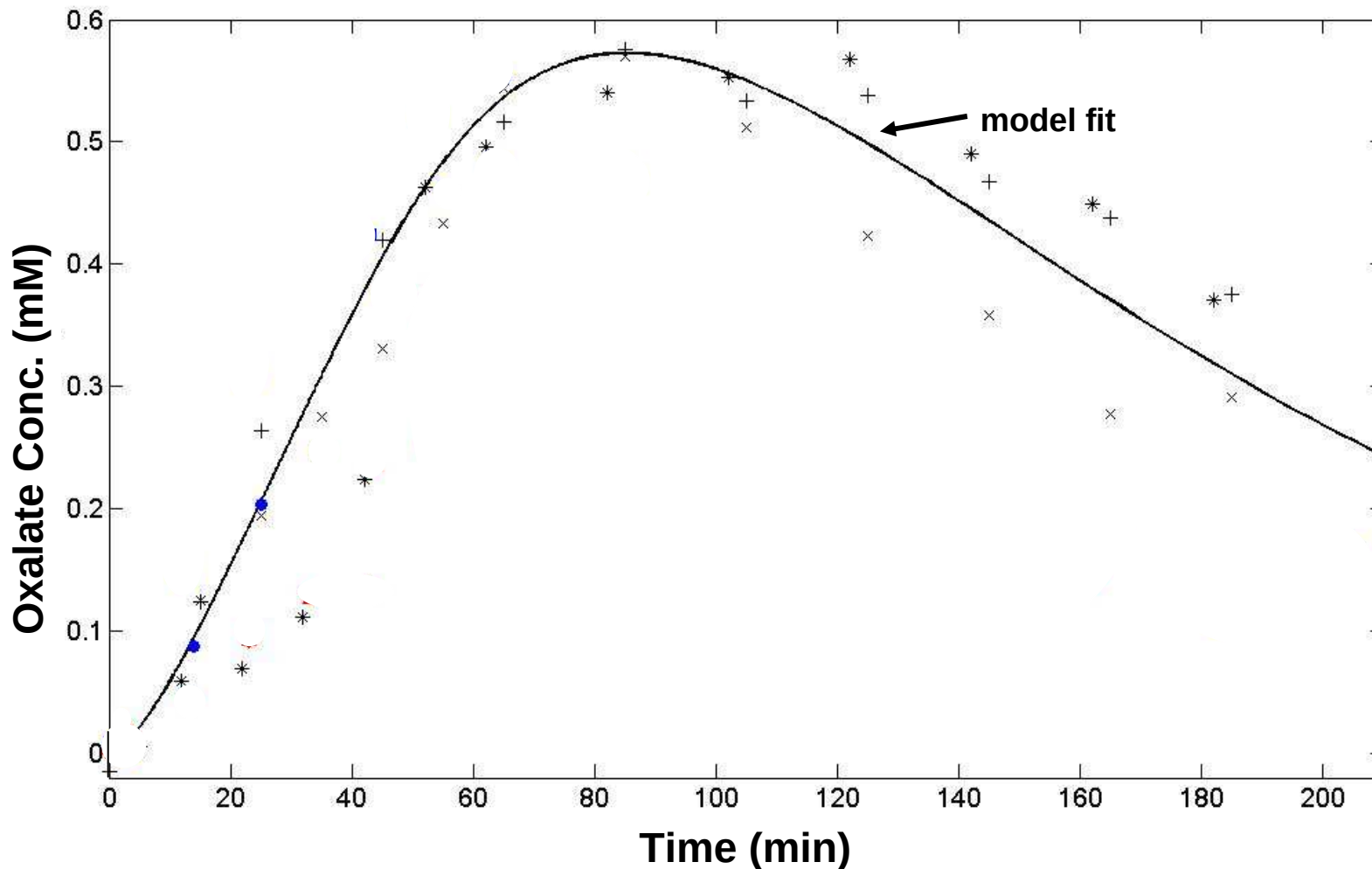
Modeling Collaborators:

Annamarie 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 + $\cdot\text{OH}$ (15 mM H_2O_2 + UV)

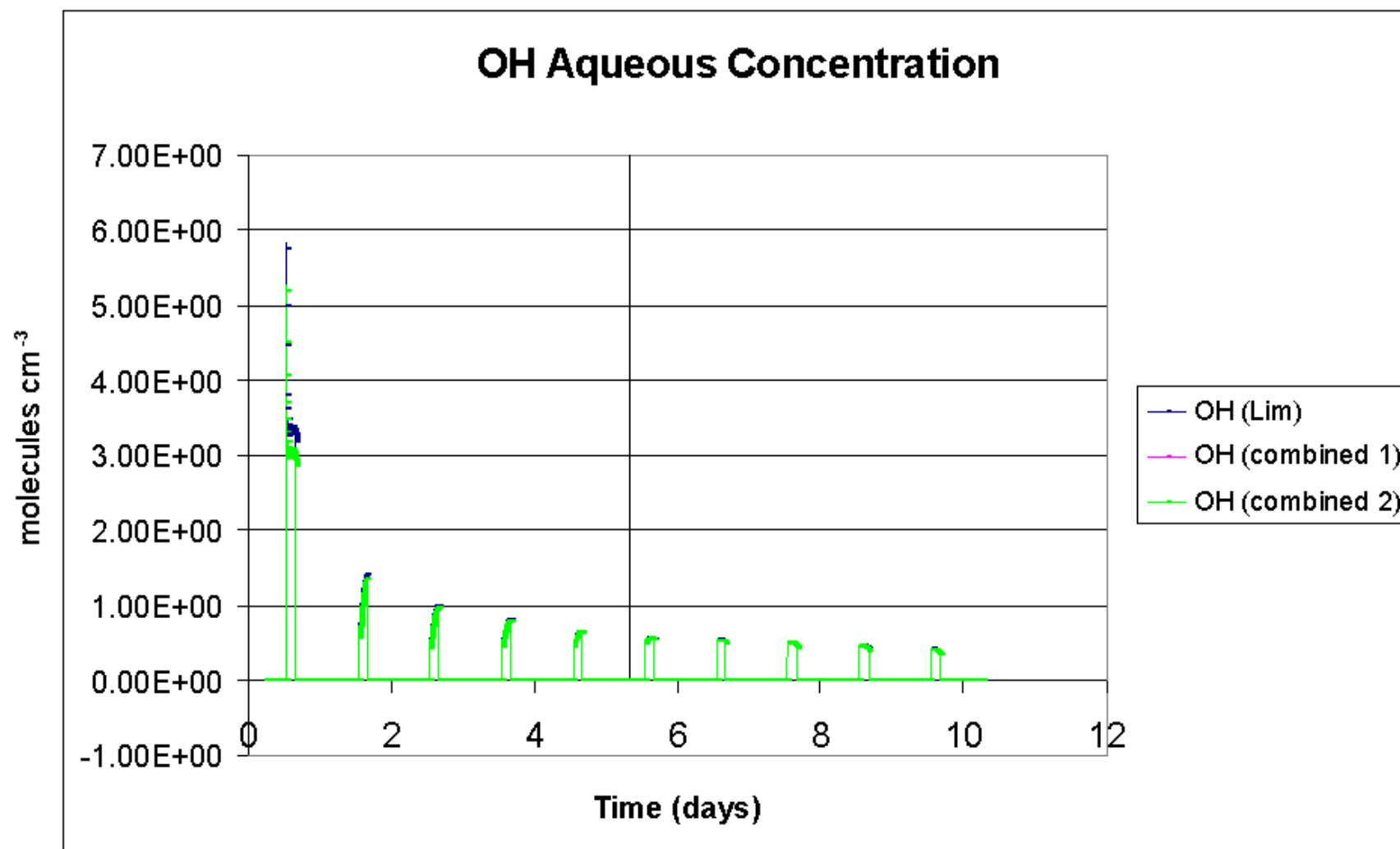


(model of Carlton et al., 2007; modified, now captures pH change)

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

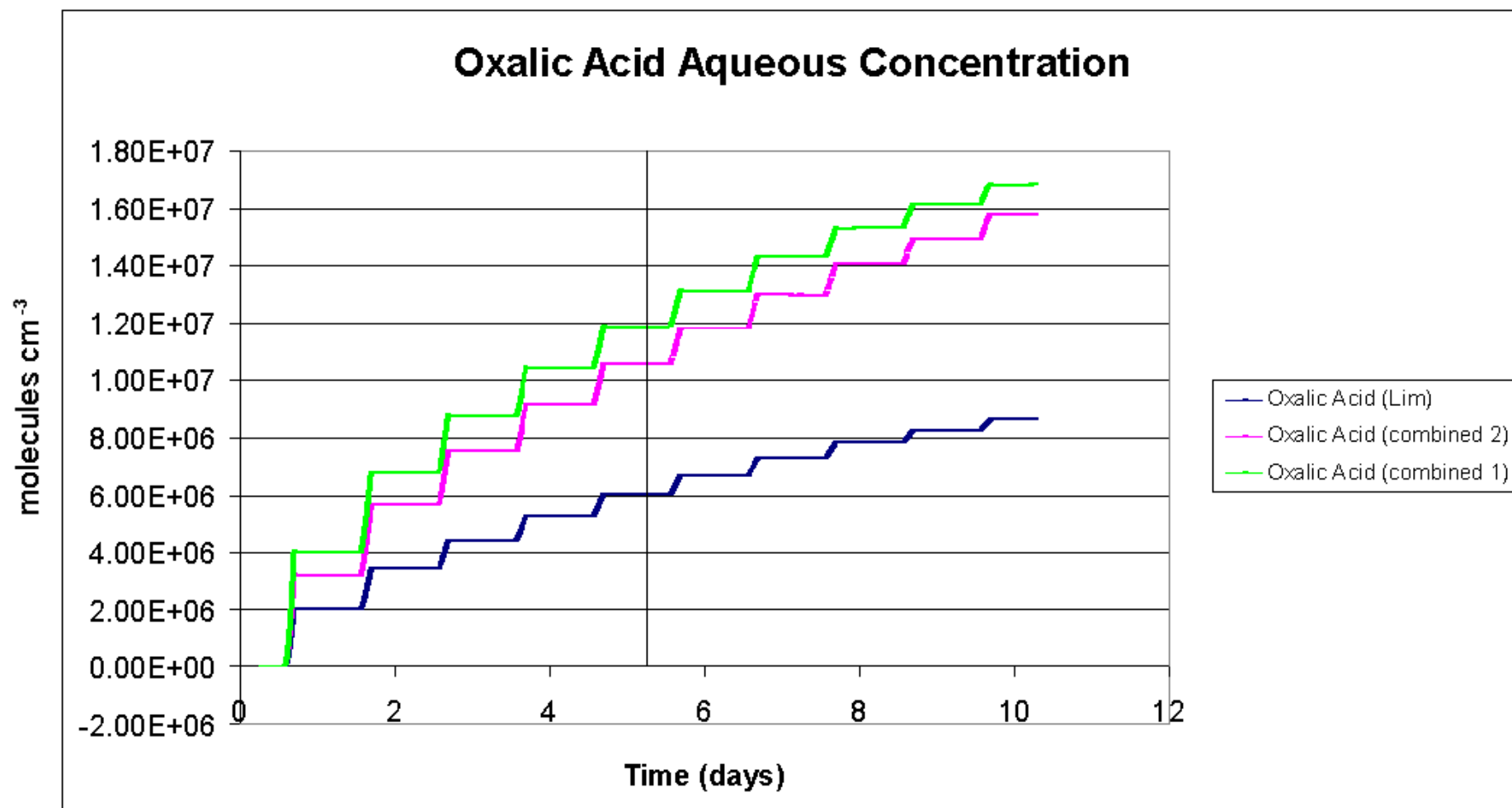
- 5 days in equatorial Amazon; 5 days in marine area
- **Intermittent clouds** between 13:00–16:00 daily
- Fair weather cumulus, 1 km, LWC=0.5 g/m³, T=285K, pH=4.5
- **Semi-sinusoidal change** of photolysis between 06:00-18:00 with a peak at noon and no nighttime photolysis
- 1-Box model (gas- and aqueous-phase chemistry, phase transfer, emission, dry deposition)
- Over 300 reactions: HO_x-NO_y-CO-CH₄-Isoprene-S-Metal-Cl-Organics
- Model predicts aqueous phase organic acids

Model improvements did not effect $\cdot\text{OH}$ predictions



NOTE: about 2/3rds of $\cdot\text{OH}$ is from gas phase. (Aqueous $\cdot\text{OH}$ formation is often neglected in cloud chemistry models)

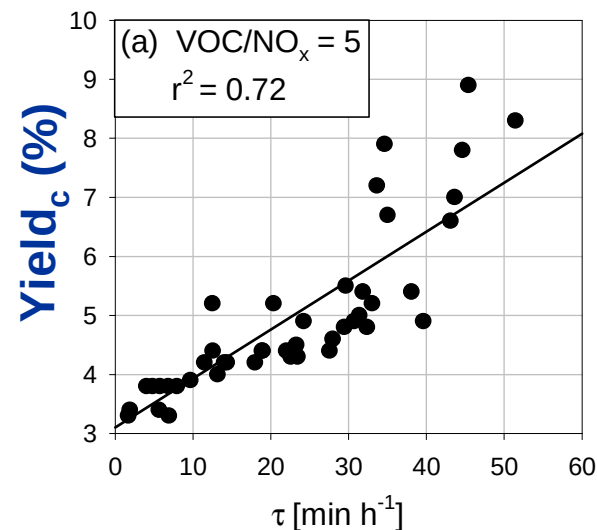
Model improvements approx. doubled oxalic acid



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

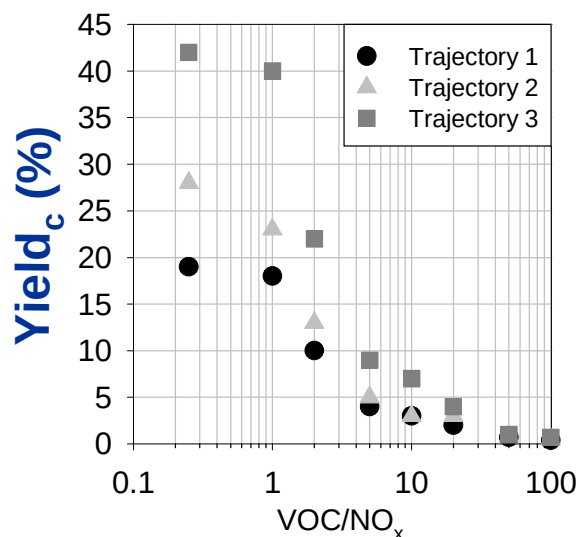
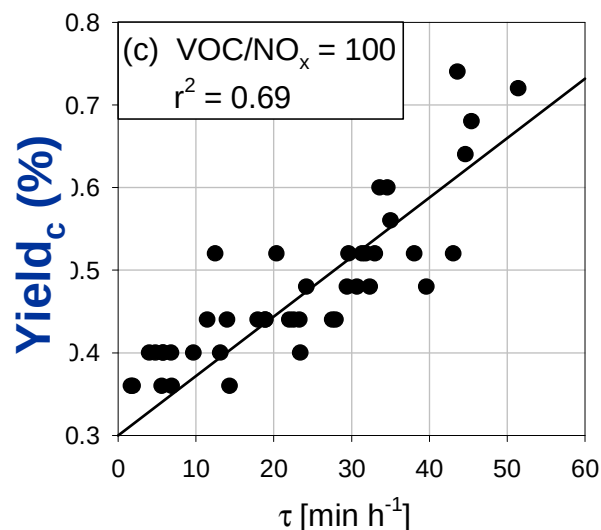


Note: higher SOA yields with higher NO_x because more gas phase production of water soluble carbonyls

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

Feingold microphys.
cloud model

VOC/NO_x



(Ervens et al., 2008)

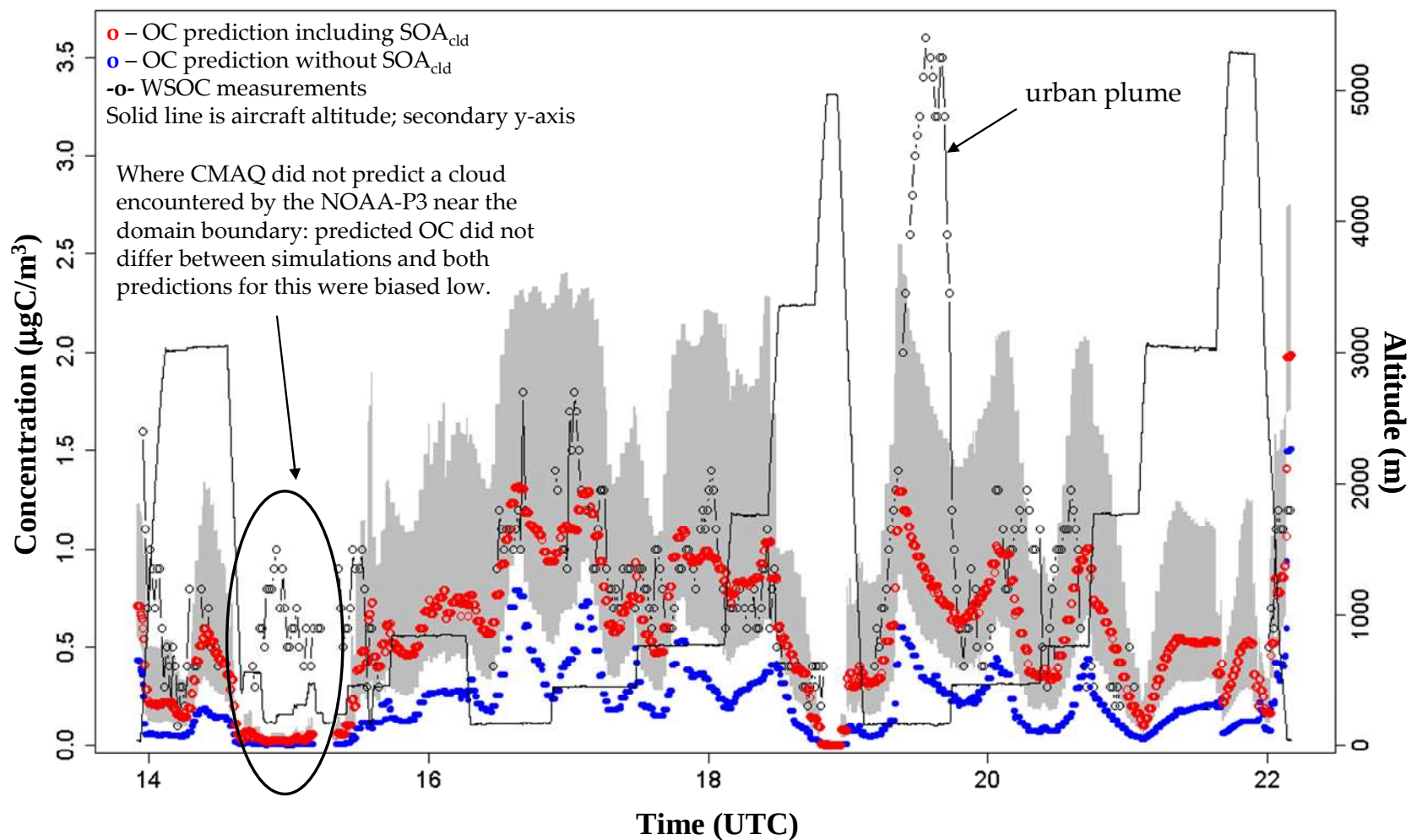
- multiple cycles
- stratocumulus
- partitioning of wsoc
- gas+aq chem
- Ervens aq chem
- altered Gly, PA chem

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%

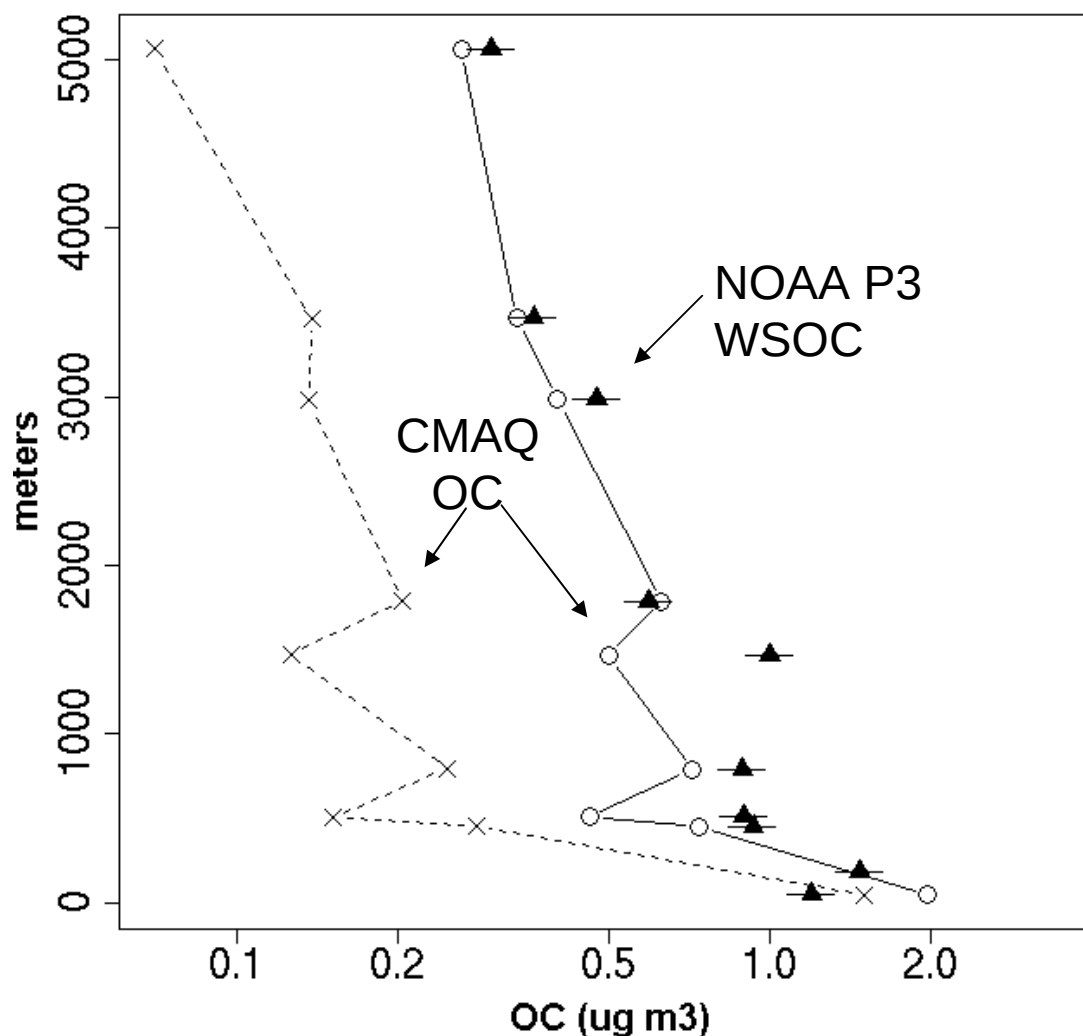


CMAQ with fixed yields from aqueous-phase aldehydes

Layer-avg conc.
Aug 14, 2004
"cloud exp"

(simulations
Aug 1-31)

In-cloud SOA
ranged from
 $0\text{--}5\text{ }\mu\text{g}/\text{m}^3$



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:

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Other Collaborators:

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