Understanding the Formation of Organic Acids via Cloud Chemistry Box Modeling

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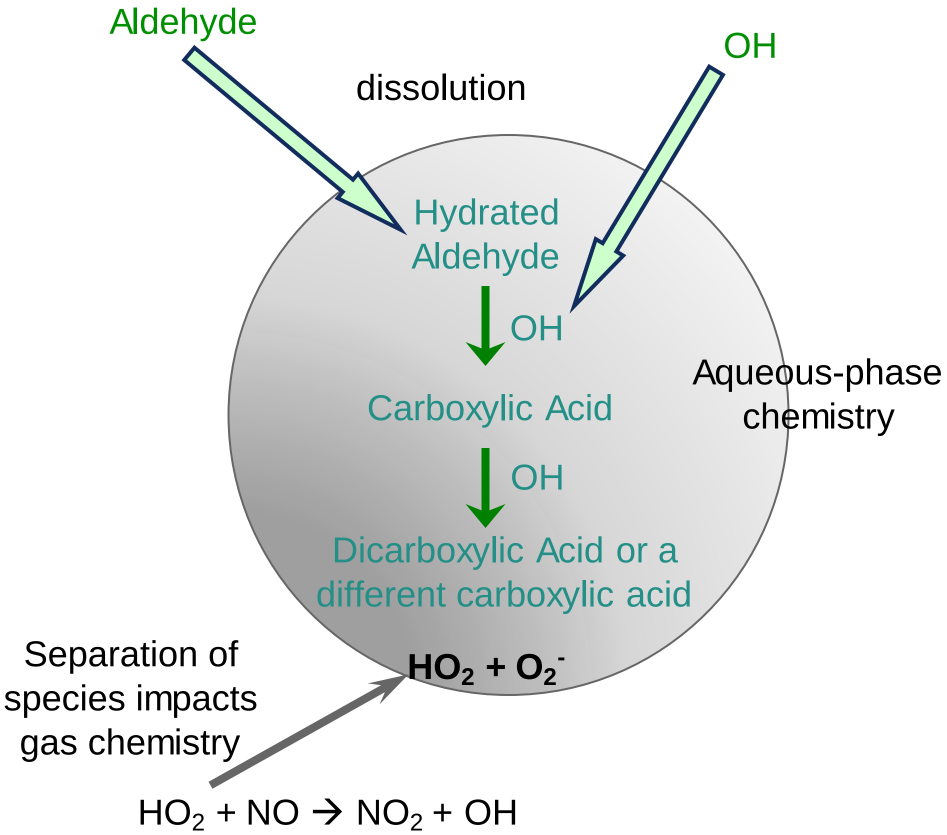
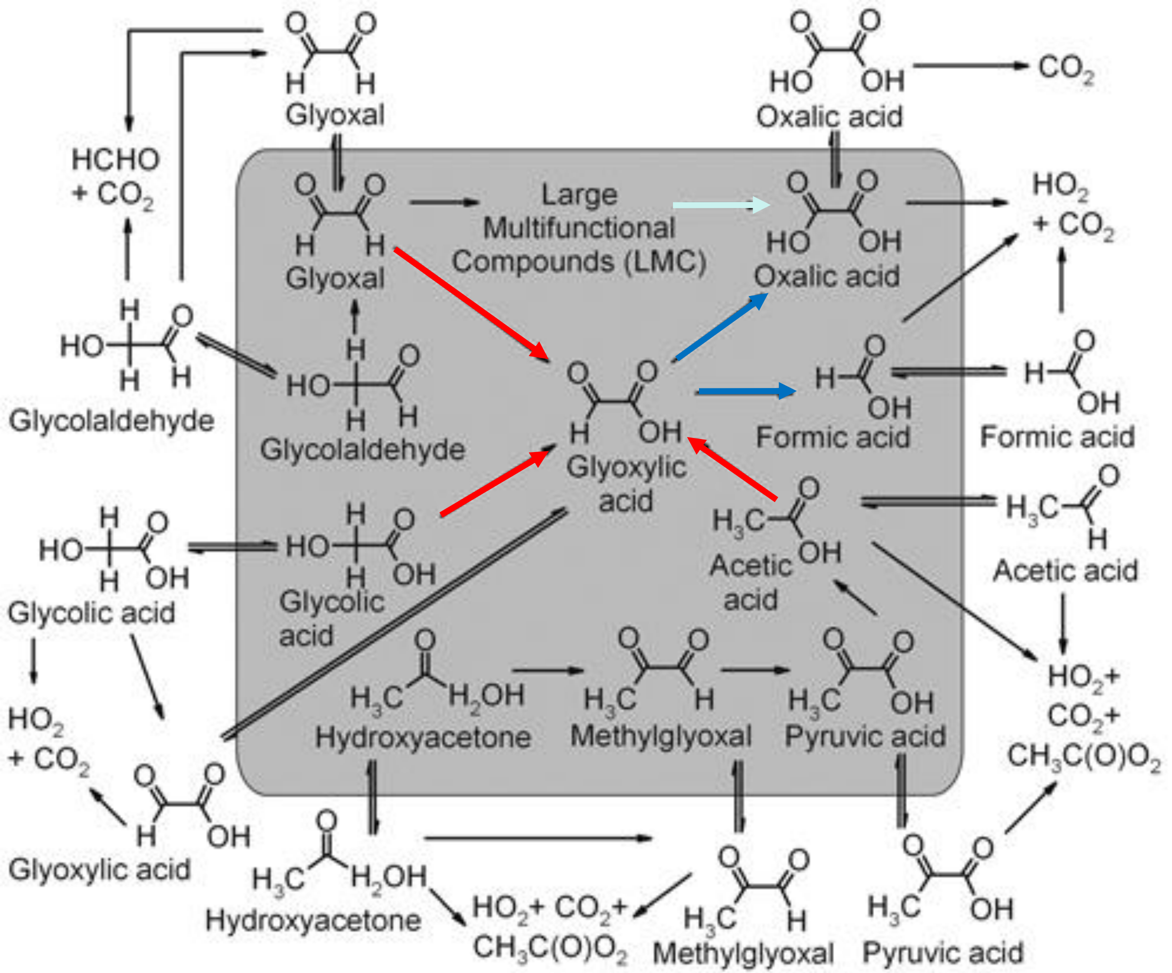
Simple Cloud Chemistry Formation of Organic Acids

Cloud Chemistry includes

- Aqueous phase chemistry
- Changes to gas chemistry due to separation of reactants
- Changes to photochemistry due to scattering by cloud



Multiphase Chemistry of Isoprene Oxidation Products



- Actually many compounds affecting formic, acetic, and oxalic acids
- Glyoxylic acid plays important role

Ervens et al. (2008) GRL

State of Knowledge of Organic Aqueous Phase Chemistry

Barth et al. (2021) compared 5 cloud chemistry box models to assess the state of knowledge of organic aqueous-phase chemistry

- Simulations at fixed point with a 20-hour cloud encounter
- Conditions for 16 September 2016

Model differences arose from

- Different chemical data used: K_H, K_1, K_2, reaction rates
- Different chemistry represented

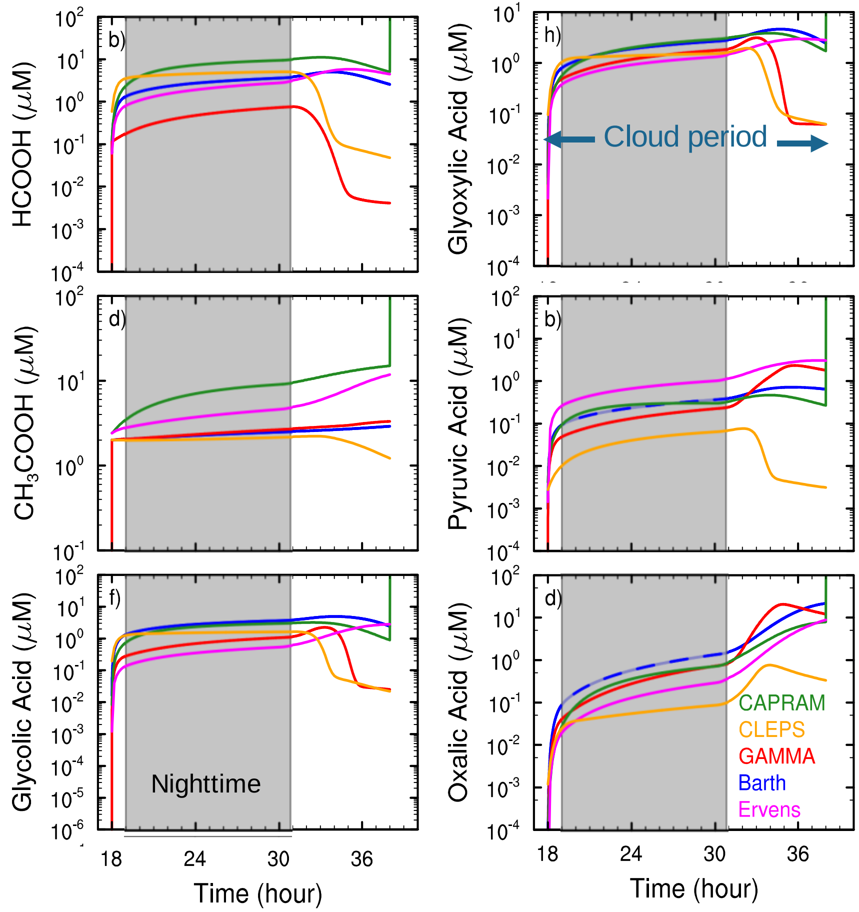
Consequently,

- Key oxidants OH and HO_2 differed
- Caused different formation rates of organic acids

Whiteface Mountain Observatory

Cloud Chemistry with prescribed pH = 4.5

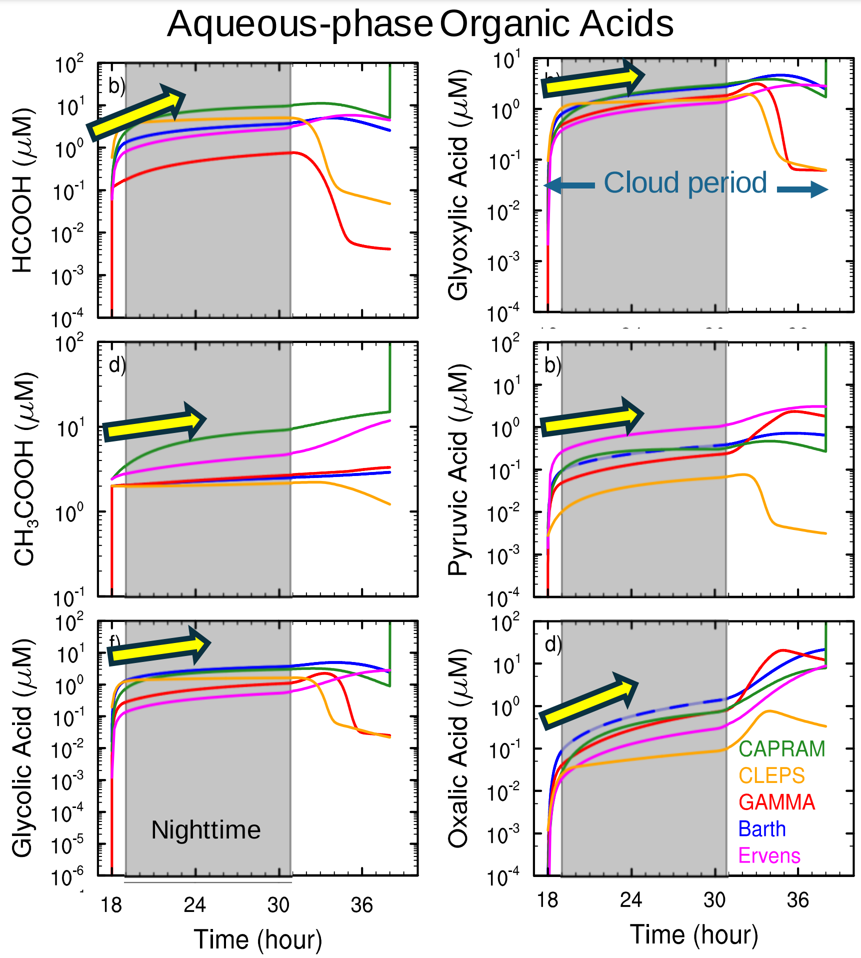
Aqueous-phase Organic Acids



Substantial variability among models in aqueous-phase organic acids

Barth et al. (2021) JGR

Cloud Chemistry with prescribed pH = 4.5



Substantial variability among models in aqueous-phase organic acids

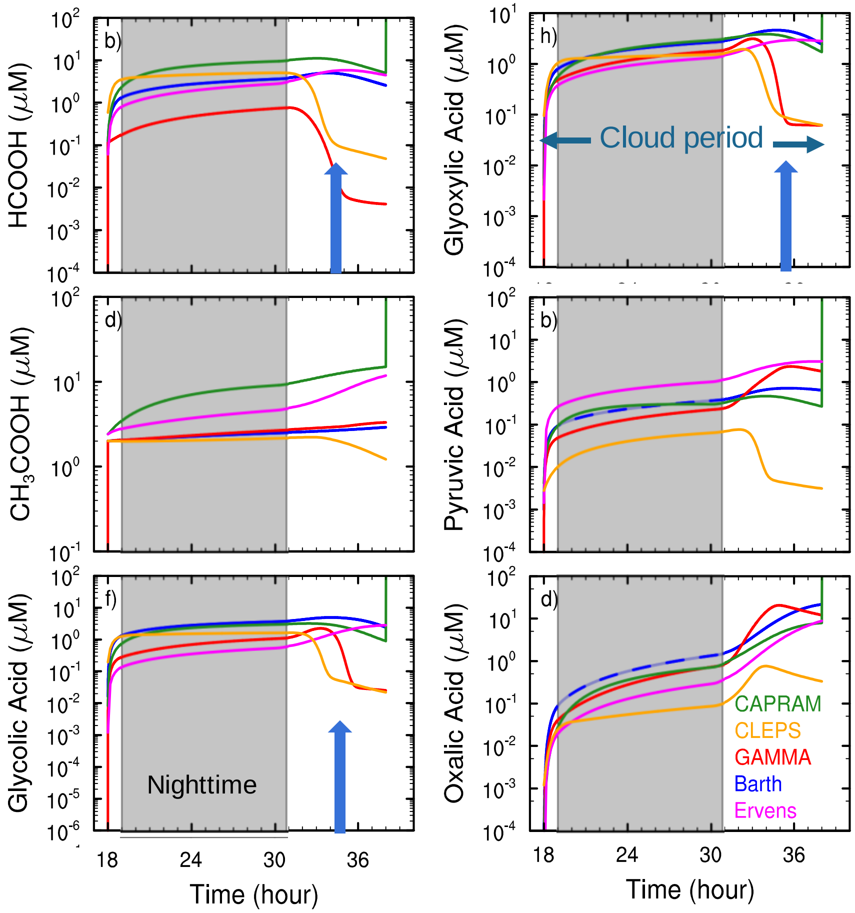
During first 3 hours all organic acids increase in concentration

- Especially HCOOH and oxalic acid

Barth et al. (2021) JGR

Cloud Chemistry with prescribed pH = 4.5

Aqueous-phase Organic Acids



Substantial variability among models in aqueous-phase organic acids

During first 3 hours all organic acids increase in concentration

During daylight of Day 2 many organic acids reach a maximum concentration and then decrease

- Dependence on OH (aq)

Barth et al. (2021) JGR

State of Knowledge of Organic Aqueous Phase Chemistry

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- **Simulations at fixed point with a 20-hour cloud encounter**
- Conditions for 16 September 2016

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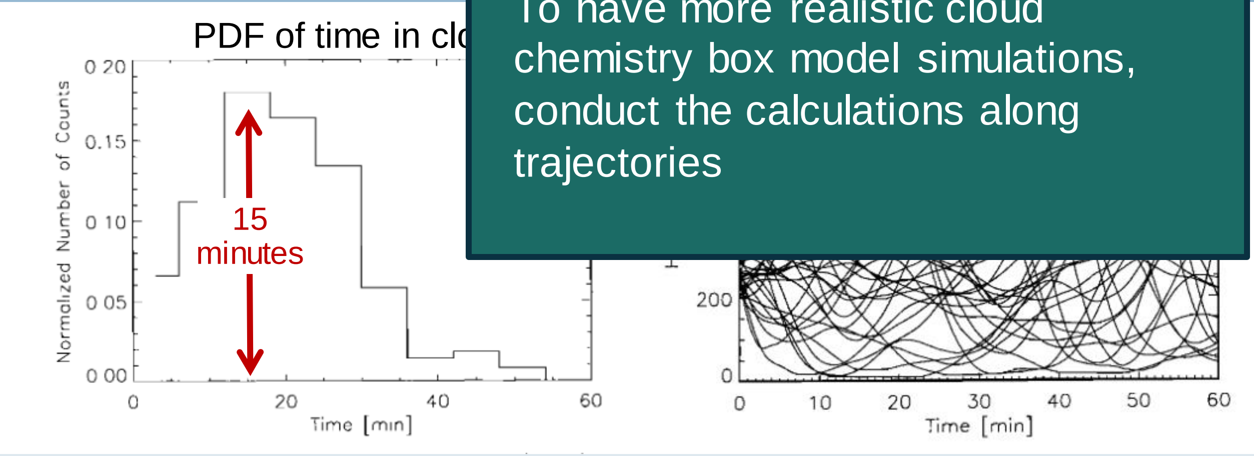
How Representative Was the Model Configuration?

- The intercomparison study provides very useful information on assessing the community's state of knowledge of cloud chemistry, but ….
- It was not a realistic simulation.
- Air parcels do not usually spend 20 hours in cloud, although one could hope that the composition of the inflow was consistent (or homogeneous) for 20 hours.

Marine Stratus / Stratocumulus:
Estimate from trajectories within a large eddy simulation
(Feingold et al., 1998, JGR)



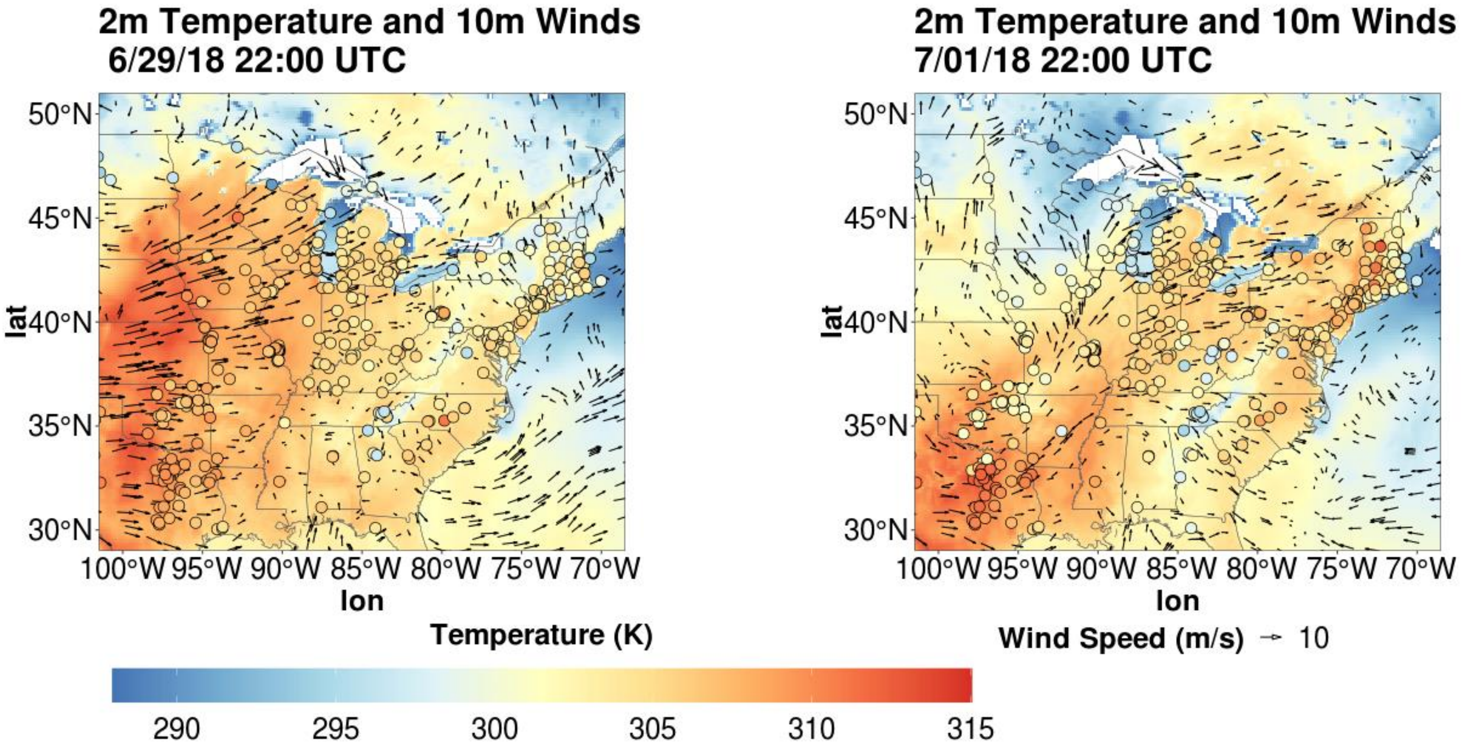
To have more realistic cloud chemistry box model simulations, conduct the calculations along trajectories

Organic Acids during a Polluted Event at Whiteface Mountain, New York

What is the role of gas-phase chemistry?
What might be the contribution of cloud chemistry?

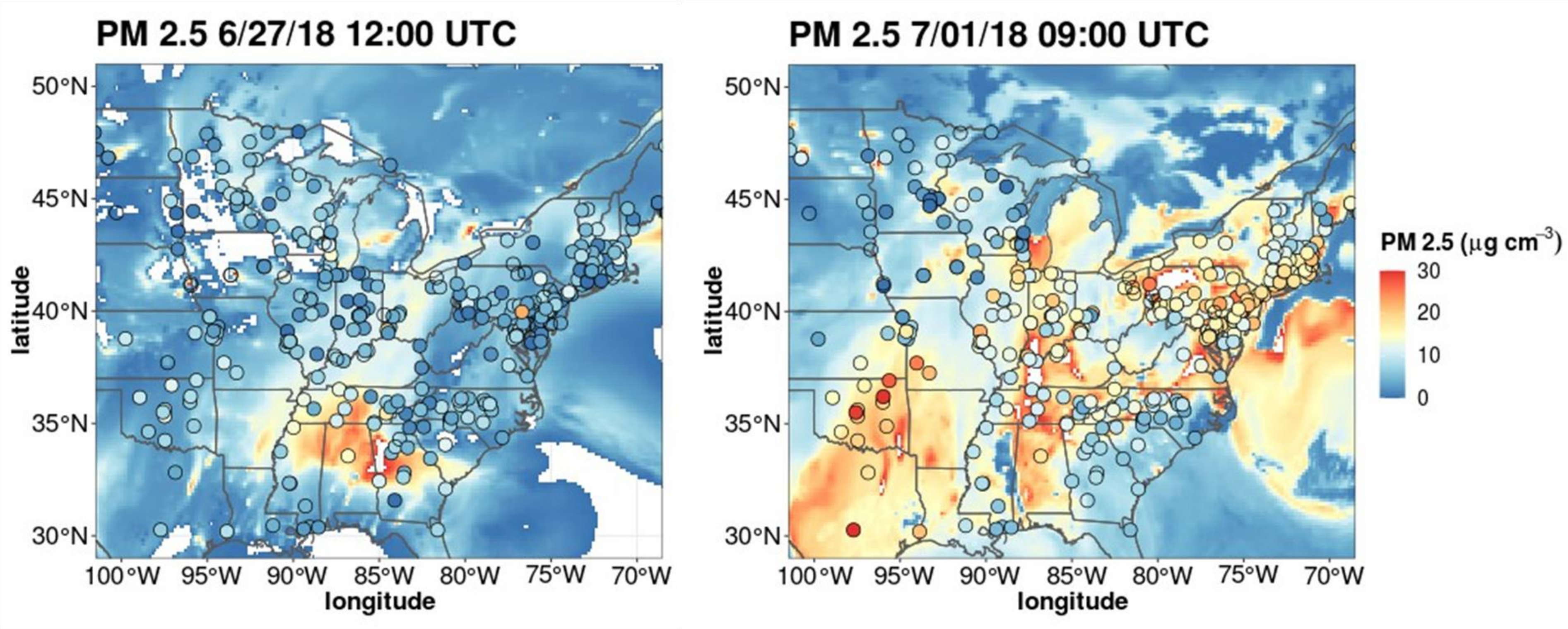
Chris Lawrence (U. Albany) is leading this work under the guidance of me and Sara Lance (U. Albany)

Heat Wave Moved into Northeast US



Maps from a simulation using the Weather Research and Forecasting (WRF) model that included observational nudging; 2-m T observations overlaid with circles

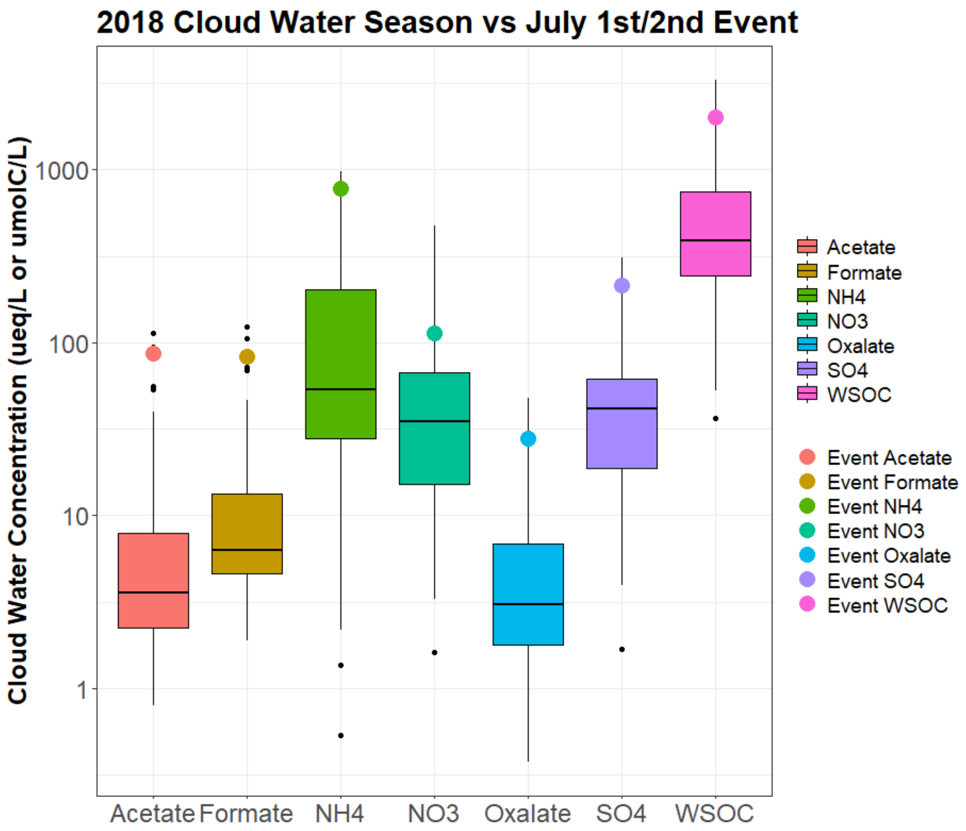
Particulate Matter Increased Substantially



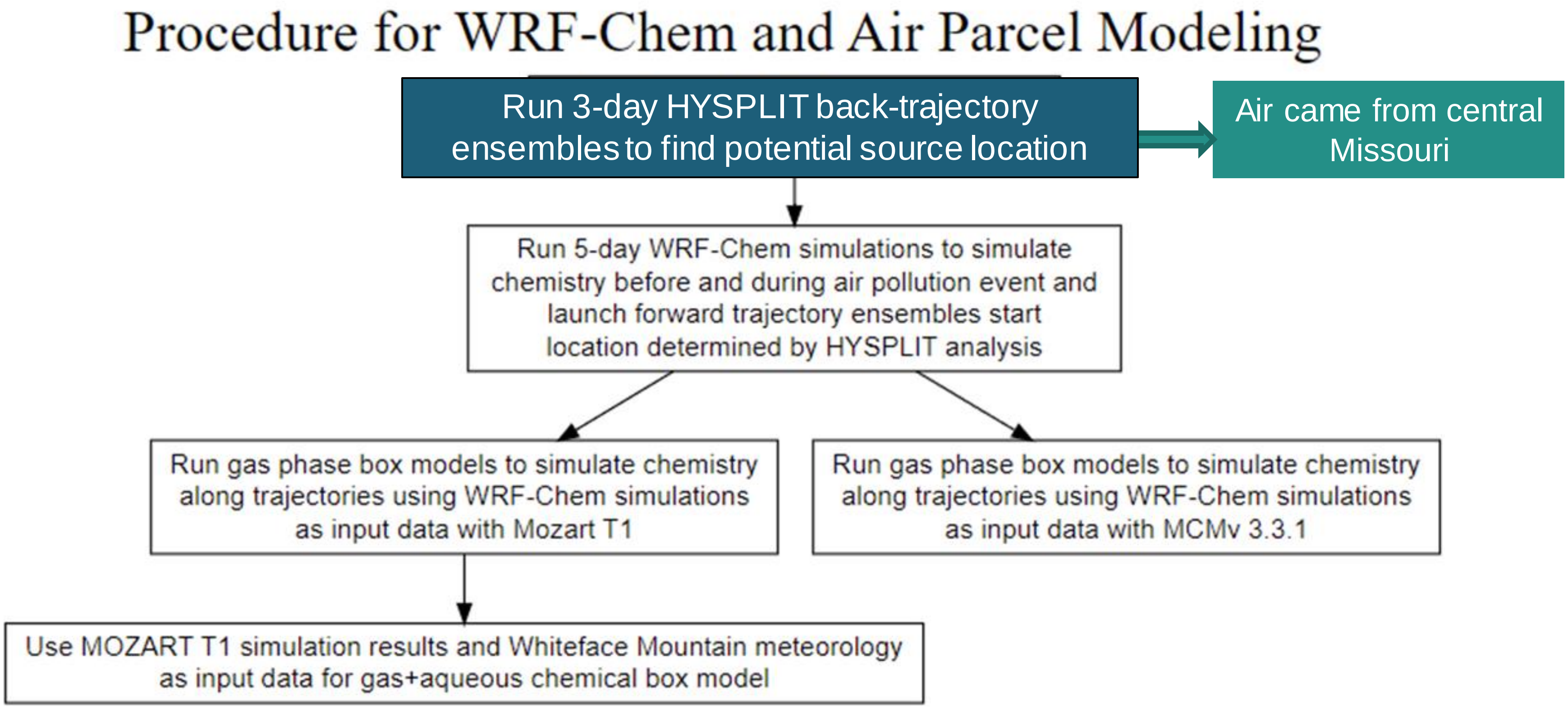
Maps from a simulation using the WRF-Chem model with EPA/Airnow observations overlaid as circles

Organic Acid Measurements at WFM since 2018

- Cloud Water Measurements at WFM
  - Inorganic anions and cations
  - TOC, WSOC
  - Organic acid anions
- Most common organic acids (2018 mean)
  - Formic acid: ~ 10 µeq/L H_2O
  - Acetic acid: ~ 5 µeq/L H_2O
  - Oxalic acid: ~ 3 µeq/L H_2O
  - Organic anions are 20 ± 20% of all anions
- 1-2 July 2018 Event (circle markers)
  - Formic acid: 83 µeq/L H_2O
  - Acetic acid: 87 µeq/L H_2O
  - Oxalic acid: 28 µeq/L H_2O



Combine WRF-Chem Modeling with Trajectory Modeling



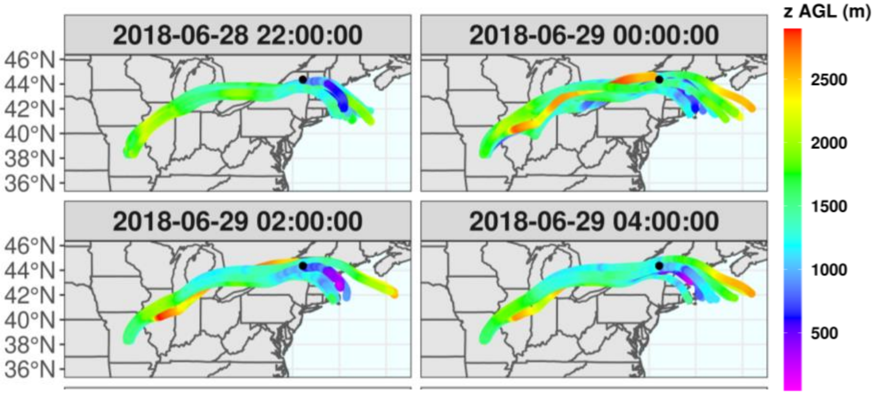
Combine WRF-Chem Modeling with Trajectory Modeling

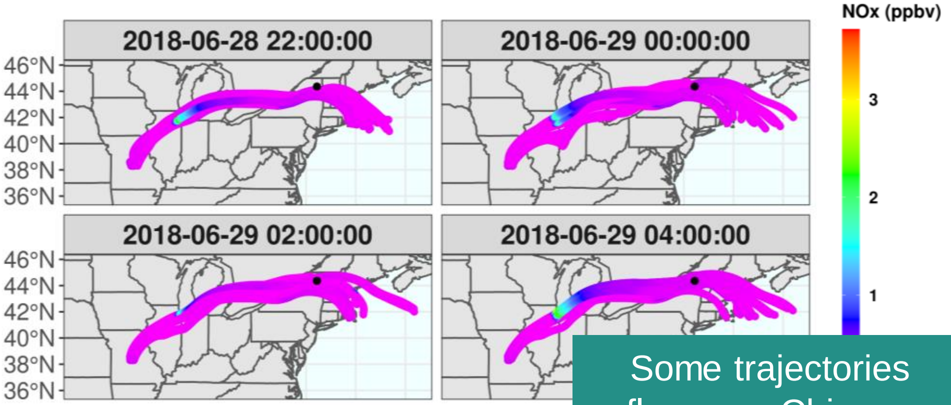
Procedure for WRF-Chem and Air Parcel Modeling

Run 5-day HYSPLIT back-trajectory ensembles to determine air mass history

Run 5-day WRF-Chem simulation for before/during air pollution event

→ Launch forward trajectories from Missouri and monitor model results along trajectories





Some trajectories flew over Chicago

Combine WRF-Chem Modeling with Trajectory Modeling

Procedure for WRF-Chem and Air Parcel Modeling

Run 5-day HYSPLIT back-trajectory ensembles to determine air mass history

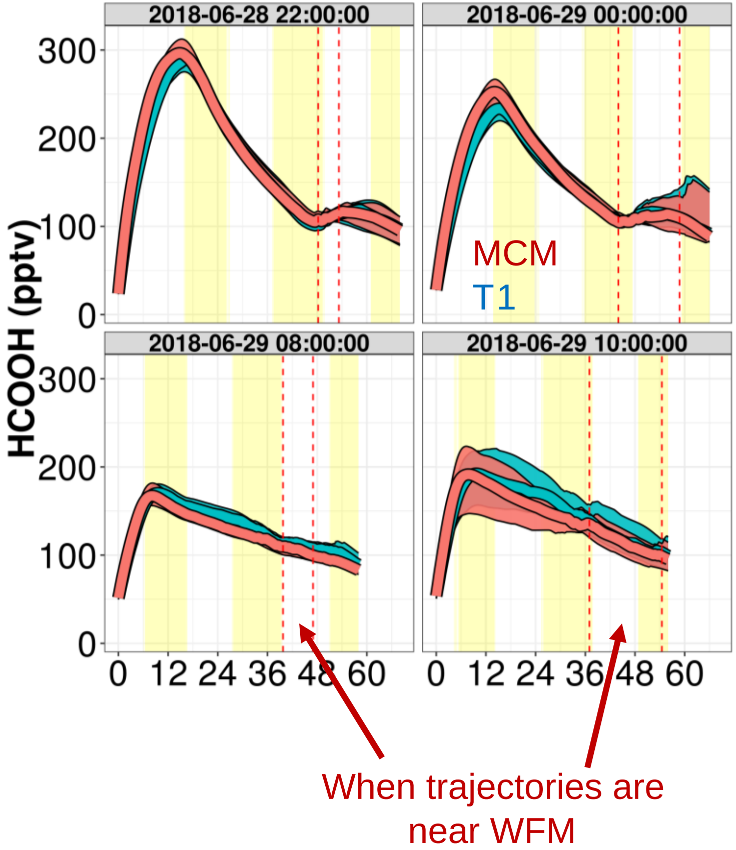
Run 5-day WRF-Chem simulations to simulate chemistry before and during air pollution event and launch forward trajectory ensembles start location determined by HYSPLIT analysis

Use WRF-Chem trajectories to prescribe initial concentrations, environmental conditions along trajectory (T, p, PBLH), emissions, and background air for mixing

→ Run BOXMOX MCM3.3.1 and MOZART-T1 gas chemistry

Use MOZART T1 simulation results and Whiteface Mountain meteorology as input data for gas+aqueous chemical box model

Formic Acid Initially Increases and then Depletes over Following 2 Days



BOXMOX simulations of formic acid

Results from MCM and T1 are comparable

Converting WFM aqueous-phase organic acid measurement to total organic acid:

$$Total\ OA = \frac{8.314 * T}{P} * LWC * OA\,(aq) + \frac{OA\,(aq)}{KH_{eff}}$$

Need > 2000 pptv formic acid

Gas-phase chemistry in these two mechanisms are not sufficient to explain measurement

Acetic Acid Initially Increases then Depletes over Following 2 Days

BOXMOX simulations of acetic acid

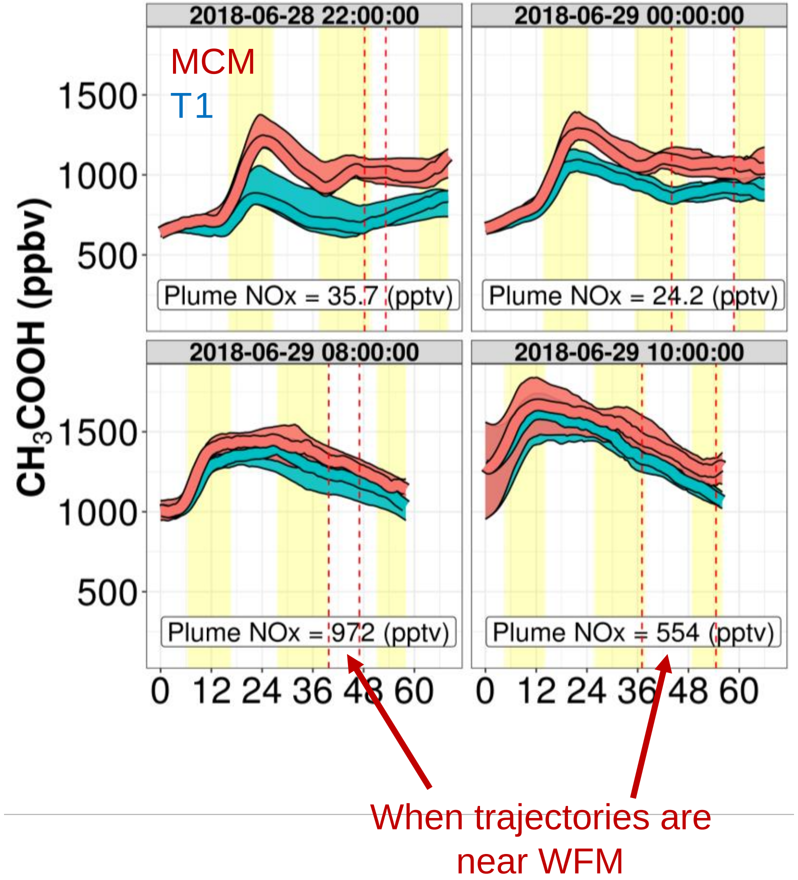
Results from MCM are somewhat larger than those from T1 due to greater CH_3CO_3 production in MCM compared to T1

Converting WFM aqueous-phase organic acid measurement to total organic acid:

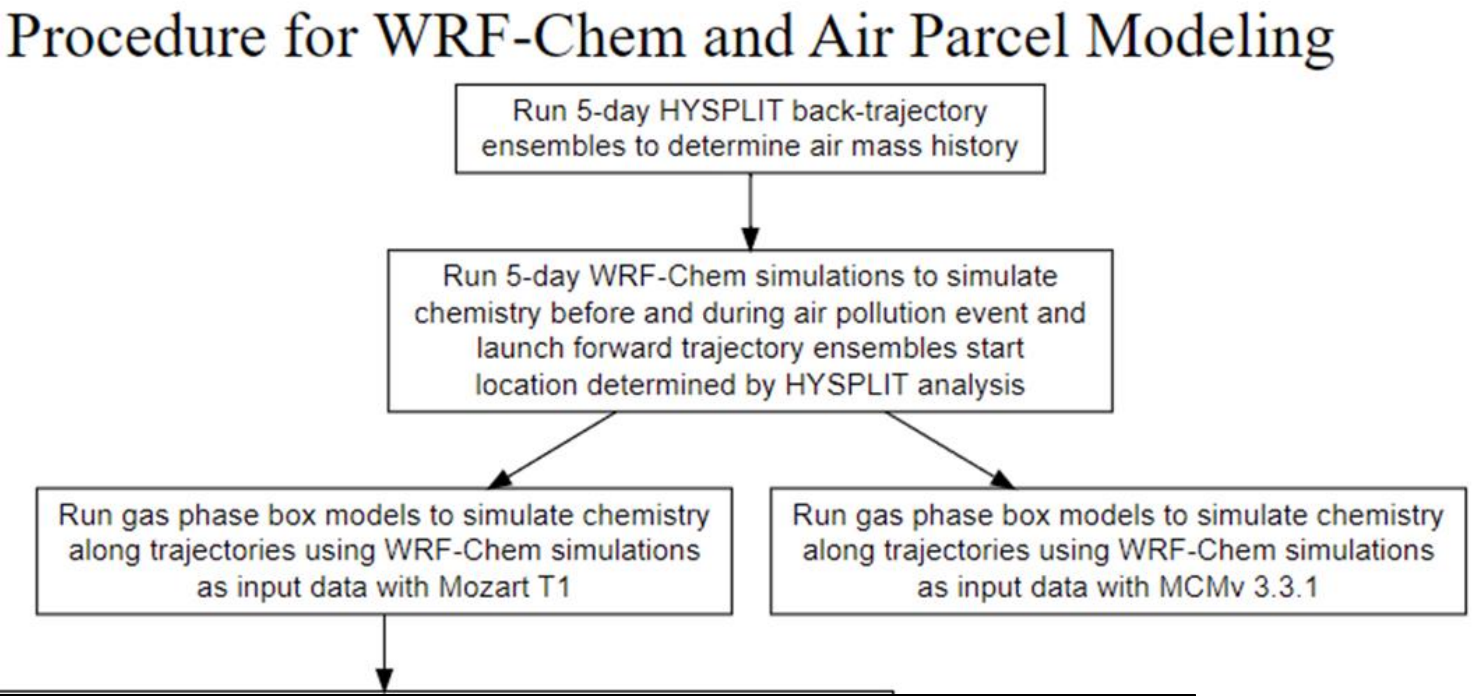
$$Total\ OA = \frac{8.314 * T}{P} * LWC * OA\,(aq) + \frac{OA\,(aq)}{KH_{eff}}$$

Need > 10,000 pptv acetic acid

Gas-phase chemistry in these two mechanisms are not sufficient to explain measurement



Combine WRF-Chem Modeling with Trajectory Modeling



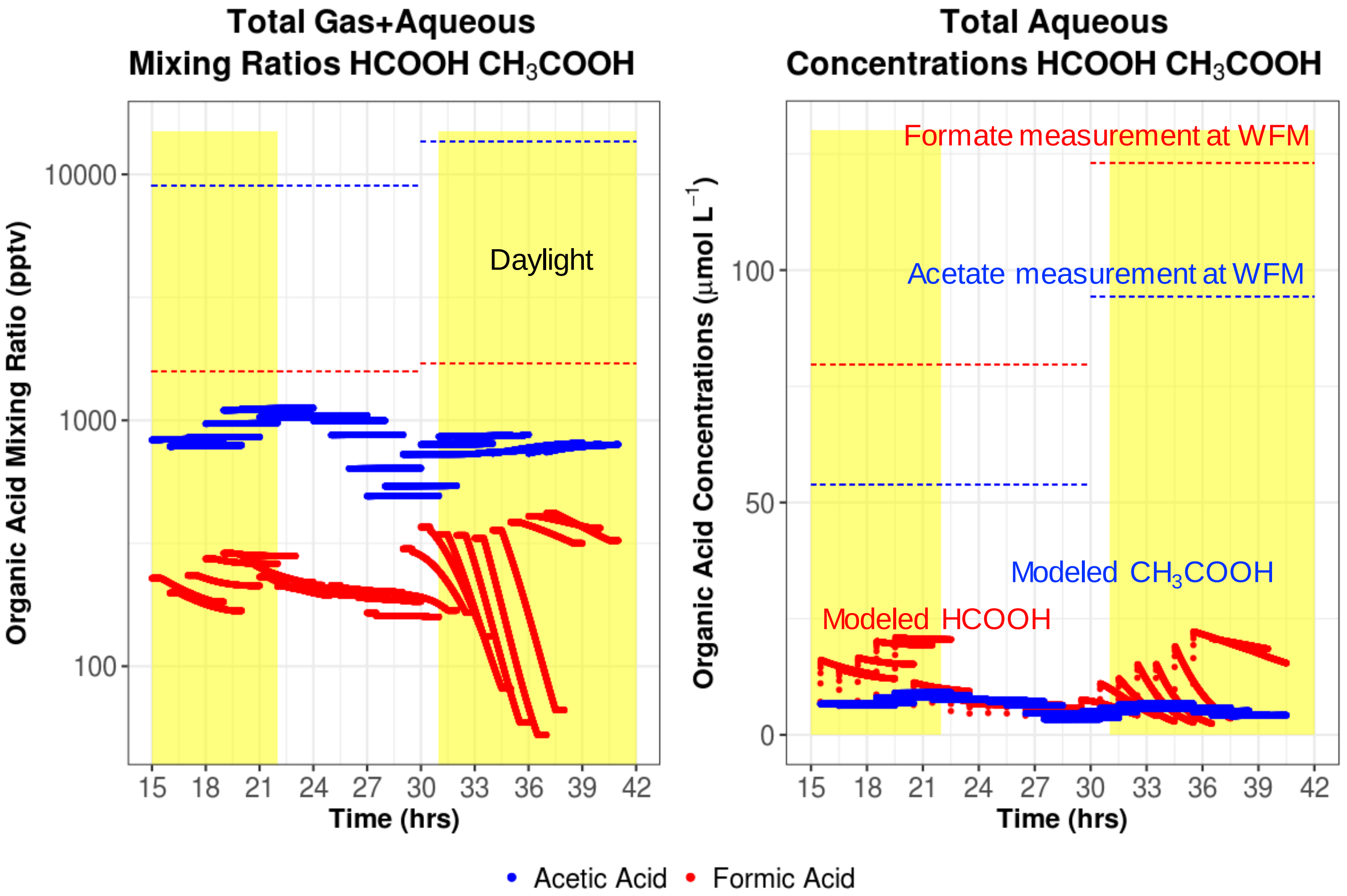
Use BOXMOX MOZART-T1 results as input for the Barth cloud chemistry model
LWC, T, P prescribed from WFM measurements
3-hour simulations

Aqueous-Phase Formic and Acetic Acids

Modeled formic acid is mostly depleted by cloud chemistry

Modeled acetic acid remains fairly constant with cloud chemistry calculations

Modeled HCOOH and CH_3COOH are much less than WFM observations

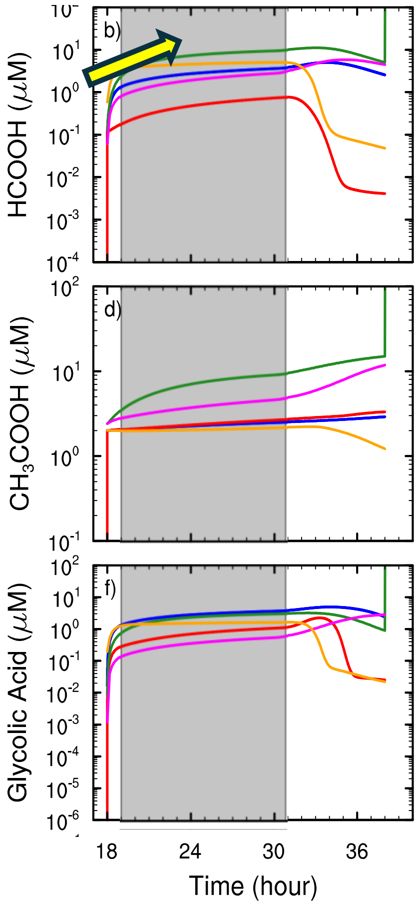


Aqueous-Phase Formic Acid Production vs Destruction

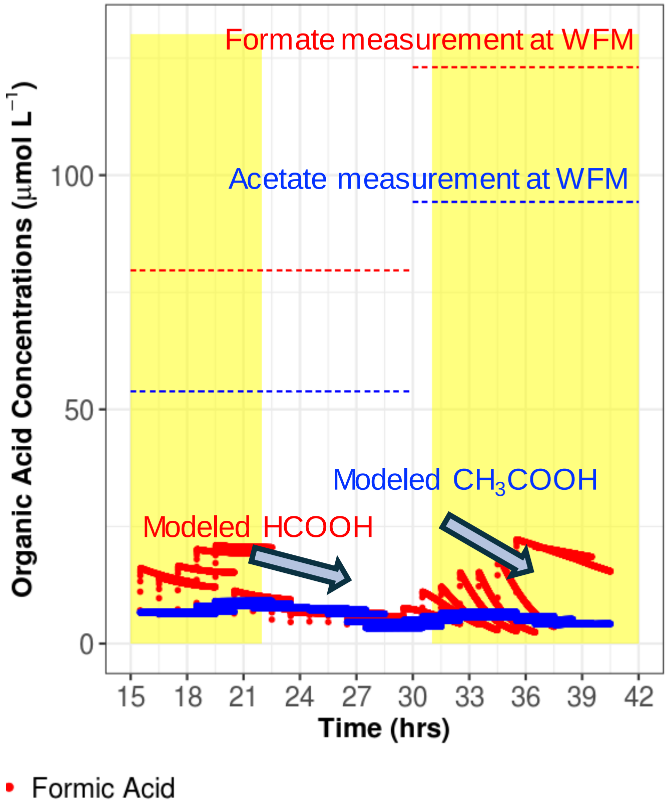
Why are there differences between the two cases?

- ➢ Initial Org. Acid – Aldehydes parameter space

September 2016 Simulation

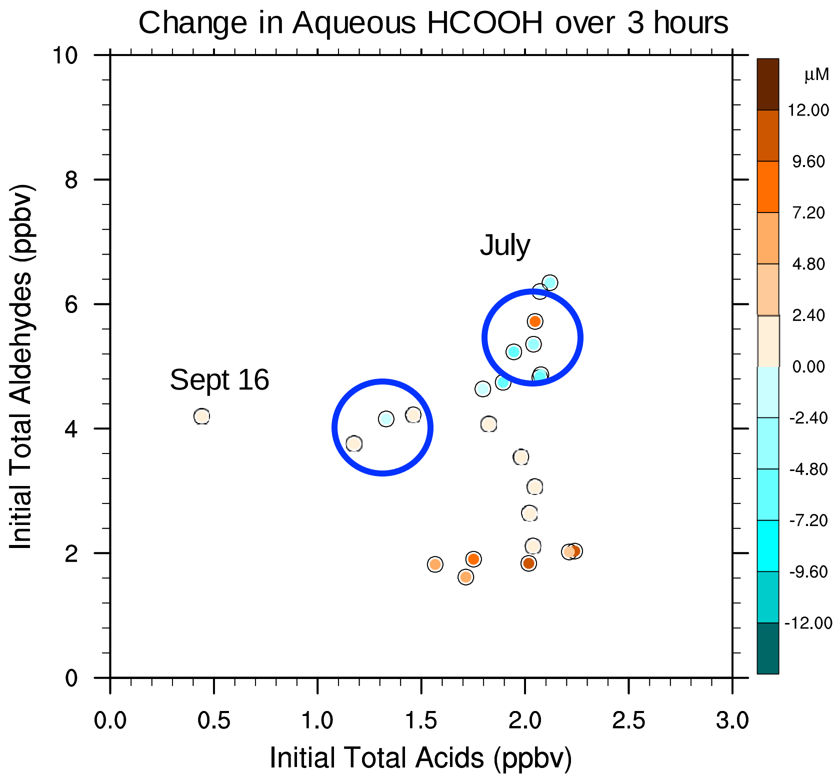


July 2018 Simulation



Aqueous-Phase Formic Acid Production vs Destruction

- Formic Acid production at lower initial aldehyde mixing ratios and lower initial organic acid mixing ratios
- The production versus destruction depends on chemical data, temperature, and likely other environmental variables (not shown)

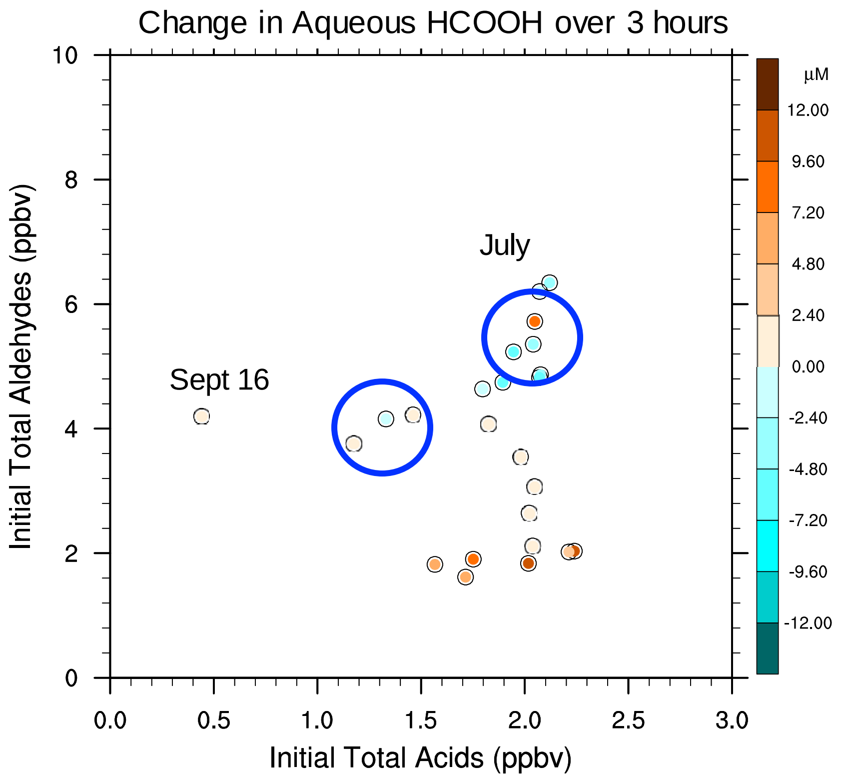


Aqueous-Phase Formic Acid Production vs Destruction

<u>Cloud Chemistry includes</u>

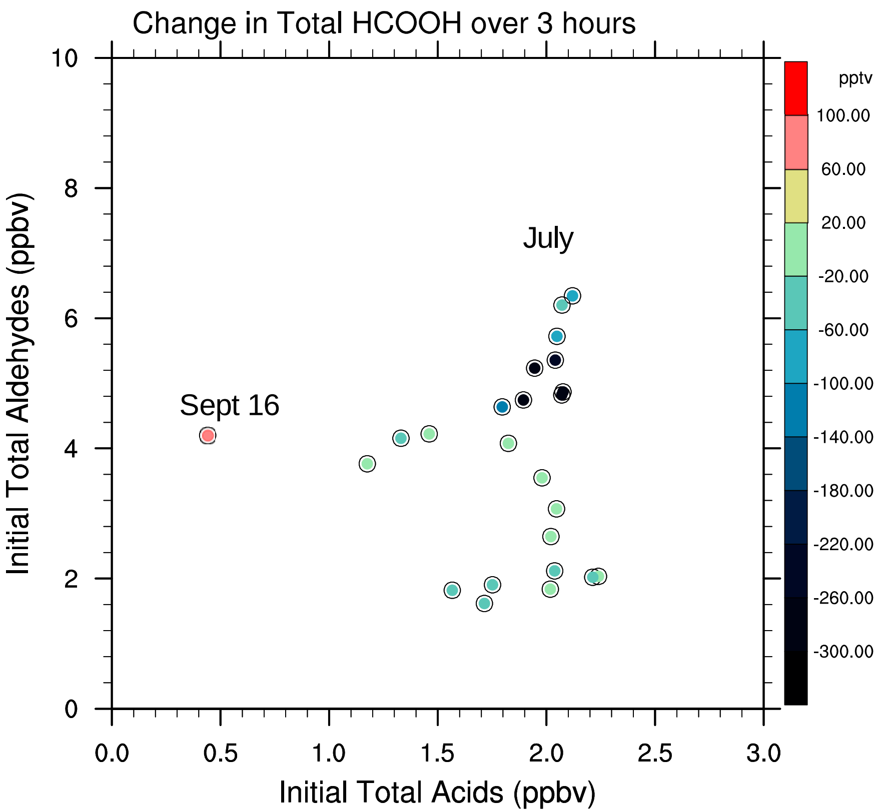
- Aqueous phase chemistry
- Changes to gas chemistry due to separation of reactants
- Changes to photochemistry due to scattering by cloud

- **But why are there some exceptions?**
  - Chemical environment: OH
  - Cloud: Liquid Water Content



Total Formic Acid Production vs Destruction

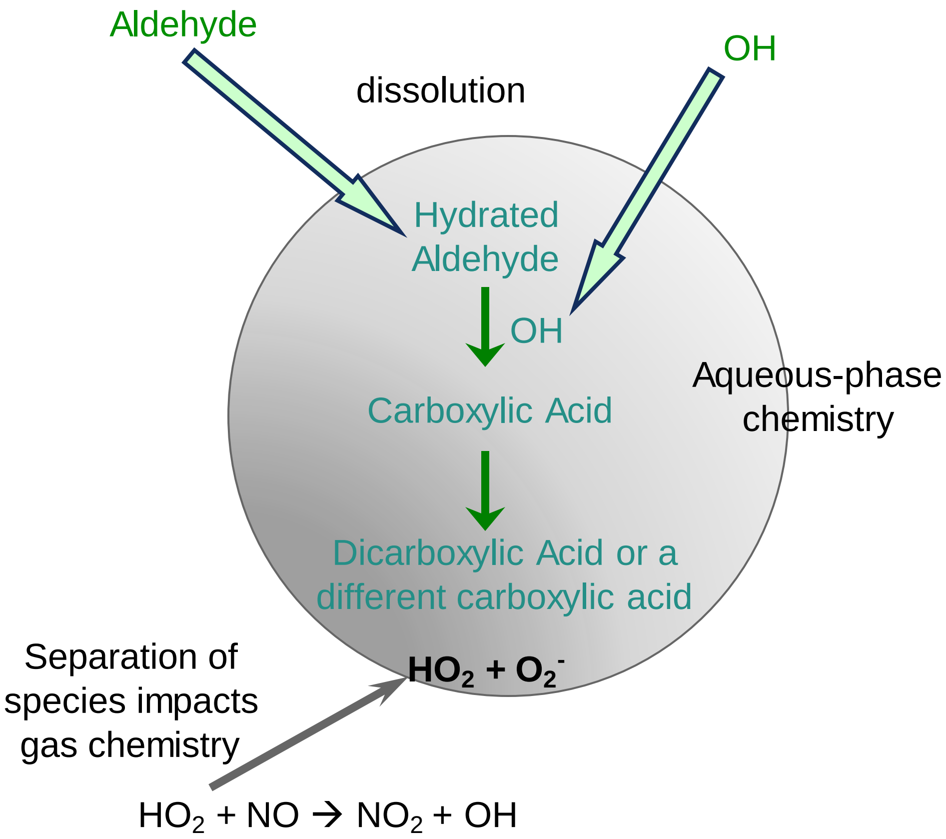
- Formic Acid production at low initial organic acid mixing ratios
- The magnitude of formic acid destruction varies with initial aldehyde mixing ratios



Conclusions

Key Points

- Important to connect the meteorology to clouds and chemistry
- Production of organic acids sensitive to choice of Henry's Law, equilibrium, and aqueous-phase reaction rate constants
- Gas-phase chemistry cannot explain measured WFM organic acids
- Future work on identifying other important organic aqueous-phase reactions is needed



Thank you!

Cloud Chemistry Needed for Oxalic Acid Production

Glyoxal produced mainly from isoprene chemistry and is a major precursor of oxalic acid

Oxalic acid production is substantial

Modeled aqueous-phase oxalic acid is mostly larger than WFM observations