ASP Science Highlight

# Overview of the Aerosol Chemistry Module
# MOSAIC

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# Objective

**Develop an aerosol chemistry module that is accurate, computationally efficient, and well-evaluated using laboratory and field measurements for inclusion in regional and global climate models**

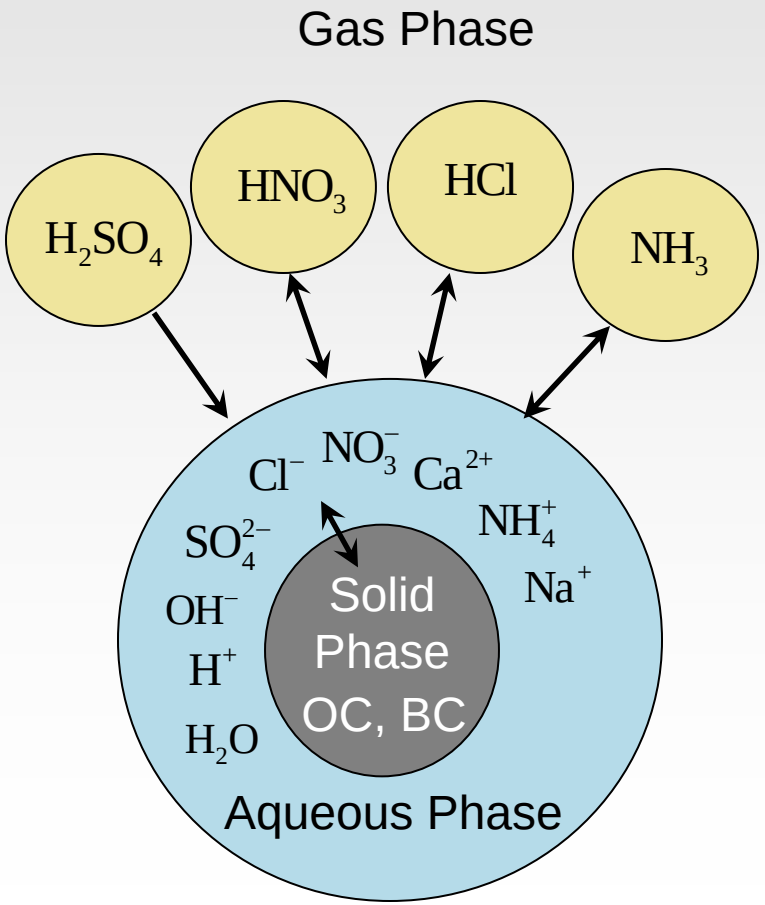
# Anatomy of a Climate Model-Worthy Aerosol Chemistry Module

**Reliable, robust, and efficient treatments for:**

- Gas-phase mechanism
- All the globally important species
- Size-resolved dynamics (modal/sectional/moments)
- Nucleation
- Thermodynamics
- Dynamic gas-particle partitioning
- Heterogeneous reactions and aerosol aging

# MOSAIC: Candidate for Climate Models

## Model for Simulating Aerosol Interactions and Chemistry




UNIQUE

**MOSAIC Sub-modules:**

- **Activity coefficients**
- **Solid-liquid equilibrium**
- **Gas-particle partitioning**

# Activity Coefficients

Multicomponent activity coefficients are needed in solid-liquid and gas-liquid partitioning calculations.

| Model or Mixing Rule | Basis | Pros and Cons |
|---|---|---|
| Bromley [1973] | Binary activity coeffs at the same ionic strength as the mixture solution | Efficient and easy to use, but accuracy deteriorates at low RH. **Most commonly used.** |
| Kusik & Meissner [1978] | | |
| Pitzer & Mayorga [1973] | Molal-scale ion interaction model | Accurate, but typically valid only up to 10-15 mol/kg |
| Pitzer-Simonson-Clegg [1986, 1998] | Mole-fraction scale ion interaction model | Highly accurate over entire RH range, but computationally too expensive |
| Metzger et al. [2002] | Mean binary activity coeffs as a fn of $a_w$ | Highly efficient, but generally not accurate below ~80% RH. |
| **MTEM**<br>**Zaveri et al. [2005]** | **Linear mixing rule for Metzger's approach** | **Efficient, easy to use, and accurate at low RH** |

# **MTEM:** Multicomponent Taylor Expansion Method

**A compact, linear mixing rule for Metzger's approach**

$$\log \gamma_A(a_w) = \sum_E \zeta_E \log \gamma^0_{A-E}(a_w)$$

where

$\log \gamma^0_{A-E}(a_w) =$ activity coeff of $A$ in a binary solution of $E$ at $a_w$

$\zeta =$ ionic mole fraction

Zaveri, R.A., R.C. Easter, and A.S. Wexler, A new method for multicomponent activity coefficients of electrolytes in aqueous atmospheric aerosols, JGR, 110, D02201, 2005.

# Bisulfate Dissociation Equilibrium

$$HSO_4^- \underset{}{\overset{K_d}{\rightleftharpoons}} H^+ + SO_4^{2-}$$

**Ionic-strength based methods such as KM, Bromley, and PSC require an iterative Bisection or Newton's method to solve this equilibrium.**

**MTEM directly gives activity coeffs at a given RH. Therefore, we only need to solve a simple quadratic eqn to obtain the equilibrium $H^+$ ion molality**

$$m_{H^+}^2 + b m_{H^+} + c = 0$$

$$b = K_d \frac{\gamma_{H_2SO_4}^3(a_w)}{\gamma_{HHSO_4}^2(a_w)} + (m_{Na^+} + m_{NH_4^+} - m_{NO_3^-} - m_{Cl^-} - m_{SULF})$$

$$c = K_d \frac{\gamma_{H_2SO_4}^3(a_w)}{\gamma_{HHSO_4}^2(a_w)} (m_{Na^+} + m_{NH_4^+} - m_{NO_3^-} - m_{Cl^-} - 2m_{SULF})$$

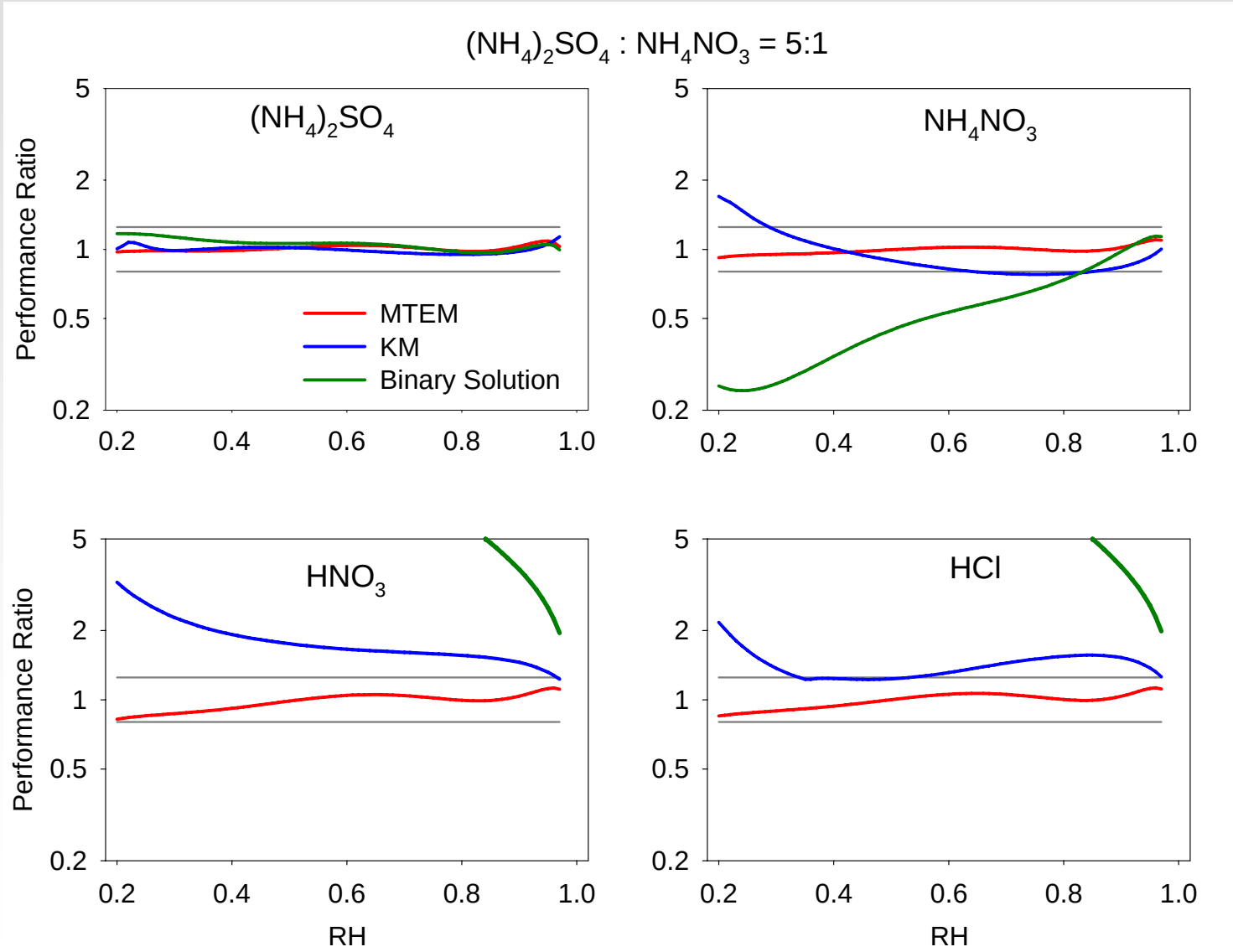
# Performance Evaluation

**Benchmark: PSC model**

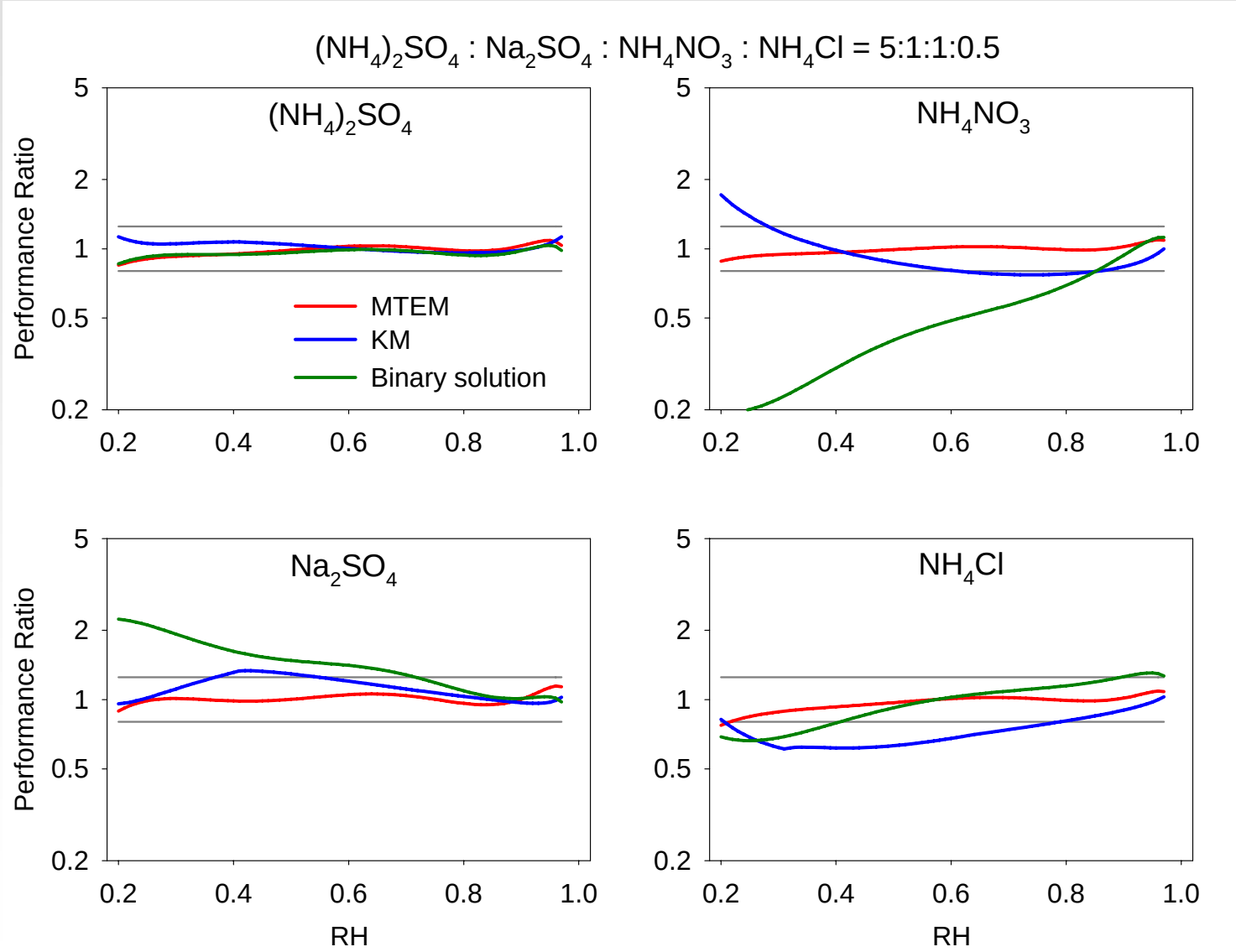
**Performance Ratio** $$\mathrm{PR}_{A,\mathrm{X}} = \frac{\gamma_A^{\mathrm{X}}(a_w)}{\gamma_A^{\mathrm{PSC}}(a_w)}$$

**X = MTEM, KM, Metzger**

# Test Case

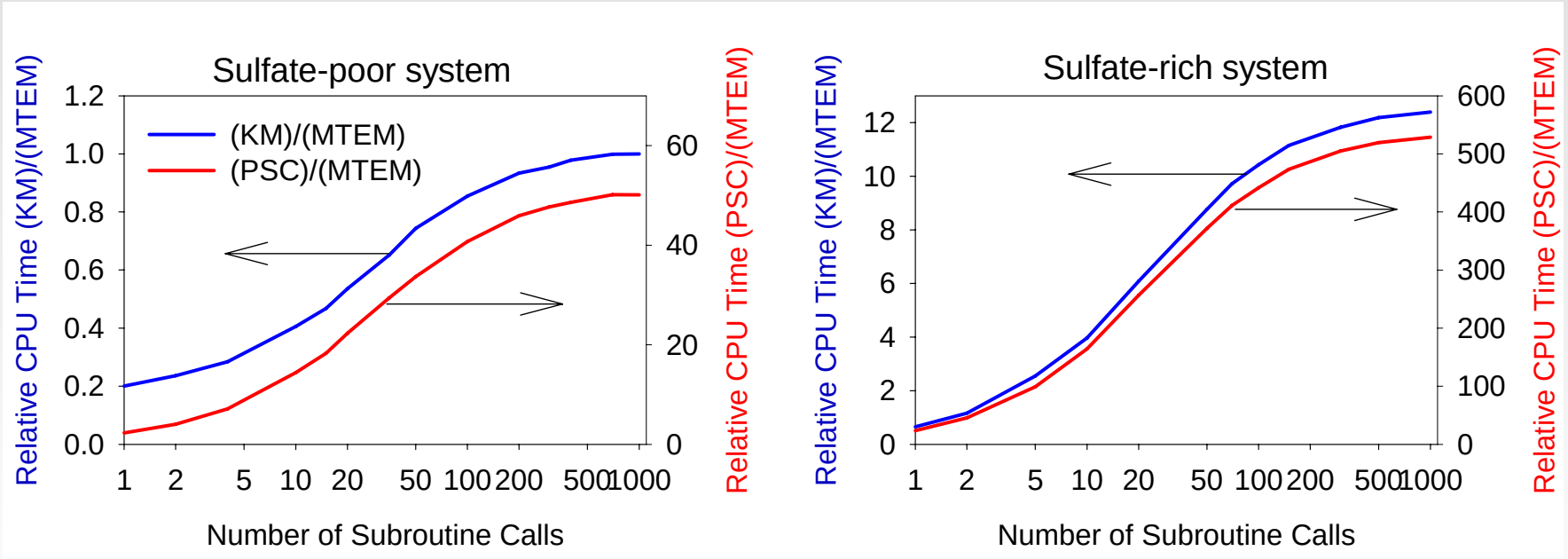

(NH4)2SO4 : NH4NO3 = 5:1
(NH4)2SO4
NH4NO3
HNO3
HCl
Performance Ratio
RH
MTEM
KM
Binary Solution
5
2
1
0.5
0.2
0.2
0.4
0.6
0.8
1.0

# Test Case


(NH4)2SO4 : Na2SO4 : NH4NO3 : NH4Cl = 5:1:1:0.5
(NH4)2SO4
NH4NO3
Na2SO4
NH4Cl
MTEM
KM
Binary solution
Performance Ratio
RH
5
2
1
0.5
0.2
0.2
0.4
0.6
0.8
1.0

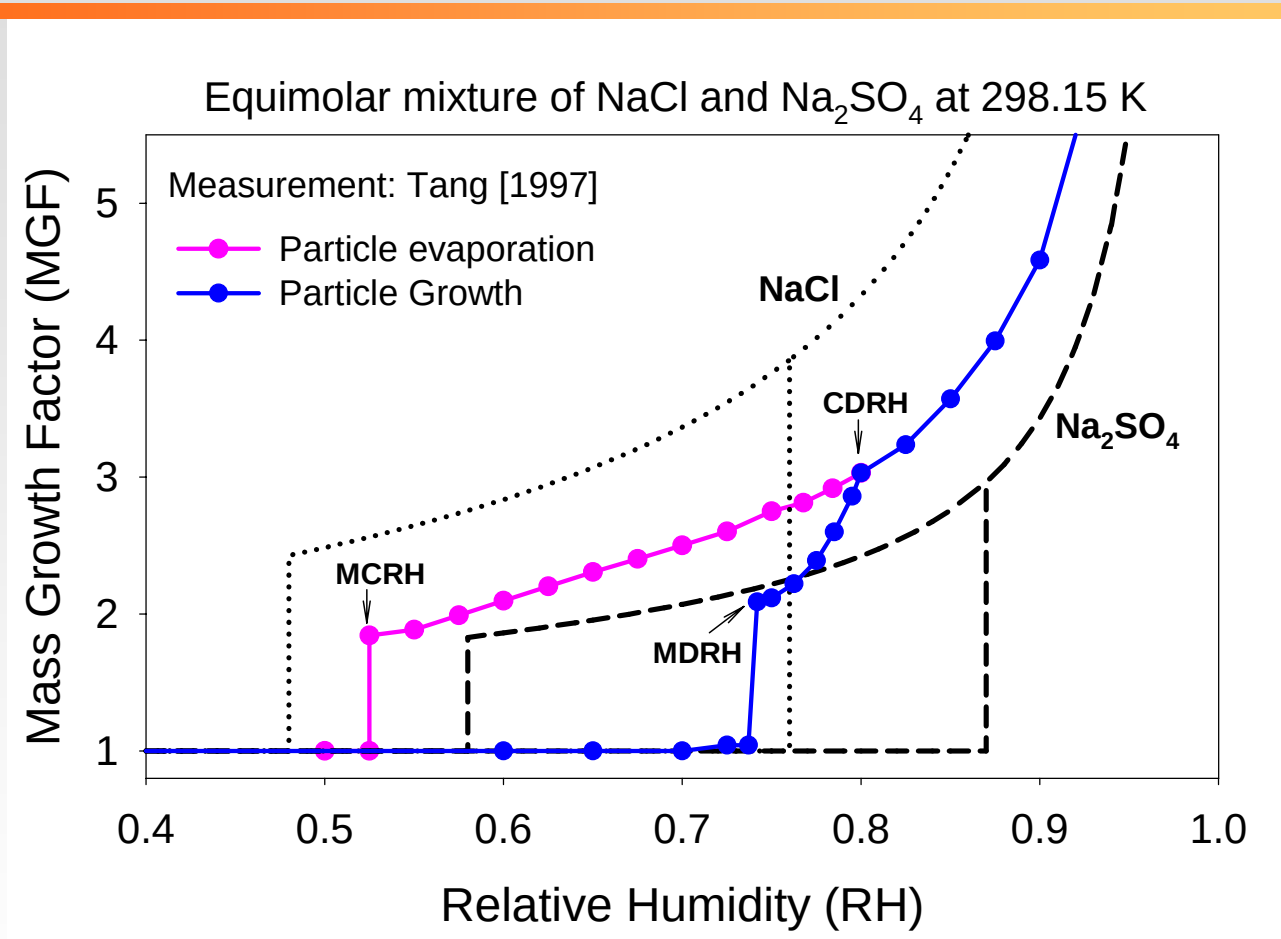
# MTEM: Computational Efficiency

## CPU requirements of MTEM w.r.t. KM and PSC




**CPU cost includes solution of bisulfate ion dissociation eqblm**

# Solid-Liquid Equilibrium




MDRH = function of which salts are present

CDRH = function of relative amounts of the salts present

# Solid-Liquid Equilibrium Solvers

| Model/Solver | Method | Pros and Cons |
|---|---|---|
| SCAPE2 & ISORROPIA | Various assumptions | Efficient at the cost of accuracy |
| EQUISOLV II | Nested iteration of equilibrium equations | Efficient and accurate |
| GFEMN & AIM2 | Direct minimization of Gibbs free energy | Very expensive but highly accurate |
| **MESA** | **Pseudo-transient Continuation (PTC) method + parameterized MDRH (lookup table)** | **Very efficient and accurate** |

# **MESA:** Multicomponent Equilibrium Solver for Aerosols

**Pseudo-Transient Continuation Technique**

Formulate the non-linear equilibrium problem as a pseudo-transient system (precipitation and dissolution) described by a set of ODEs, and solve it to steady-state to obtain the equilibrium solution.

$$E_{(s)} \underset{k_p}{\overset{k_d}{\rightleftharpoons}} \nu_M M_{(l)} + \nu_X X_{(l)}$$

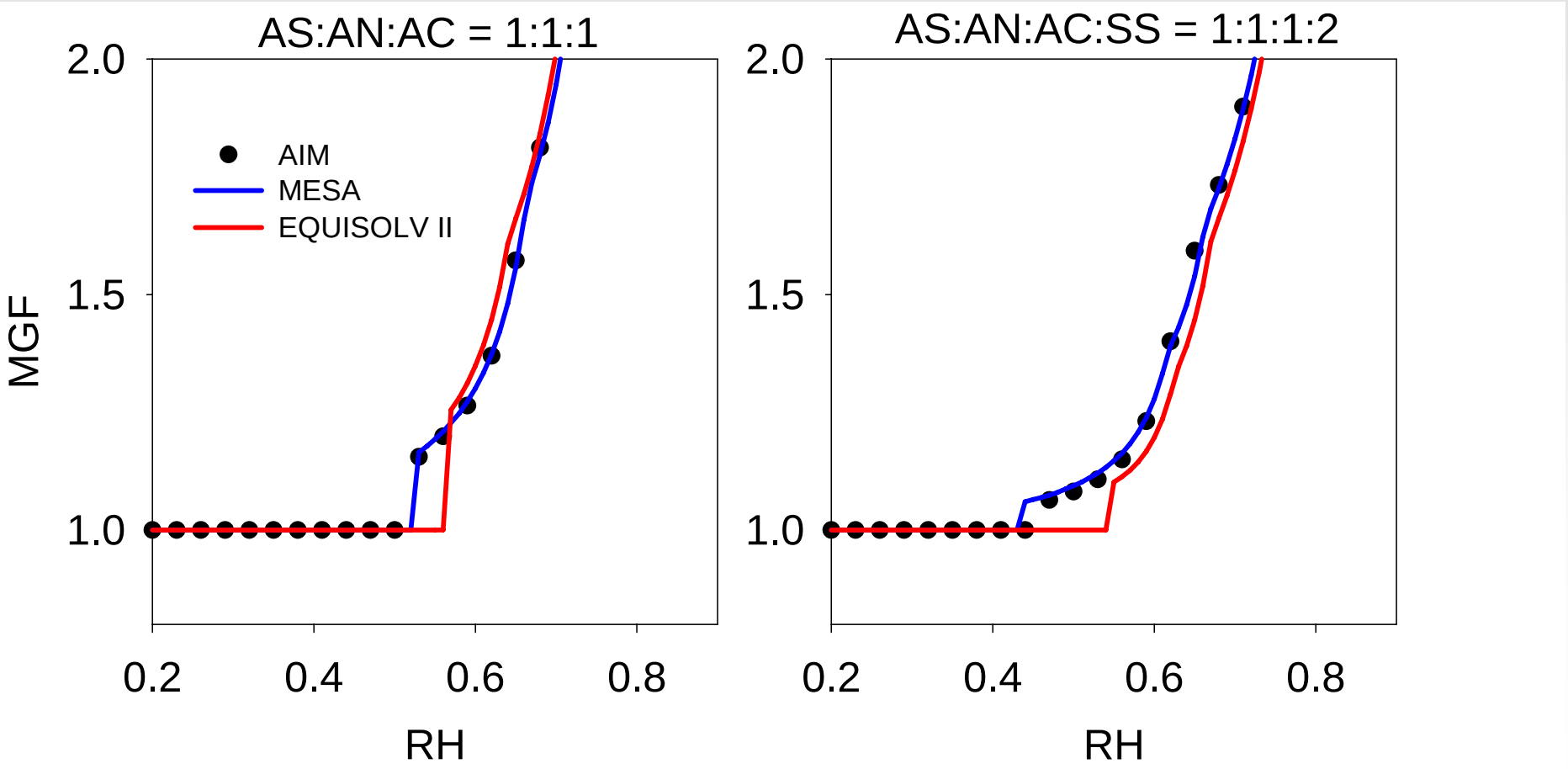
$$K_E^{sl} = k_d / k_p$$

→MDRH(T) = parameterized as a function of particle composition. Therefore, no need to solve below MDRH.

Zaveri, R.A., R.C. Easter, and L.K. Peters, A computationally efficient multicomponent equilibrium solver for aerosols (MESA), JGR, in press, 2005.

# MESA Accuracy Using AIM as Benchmark

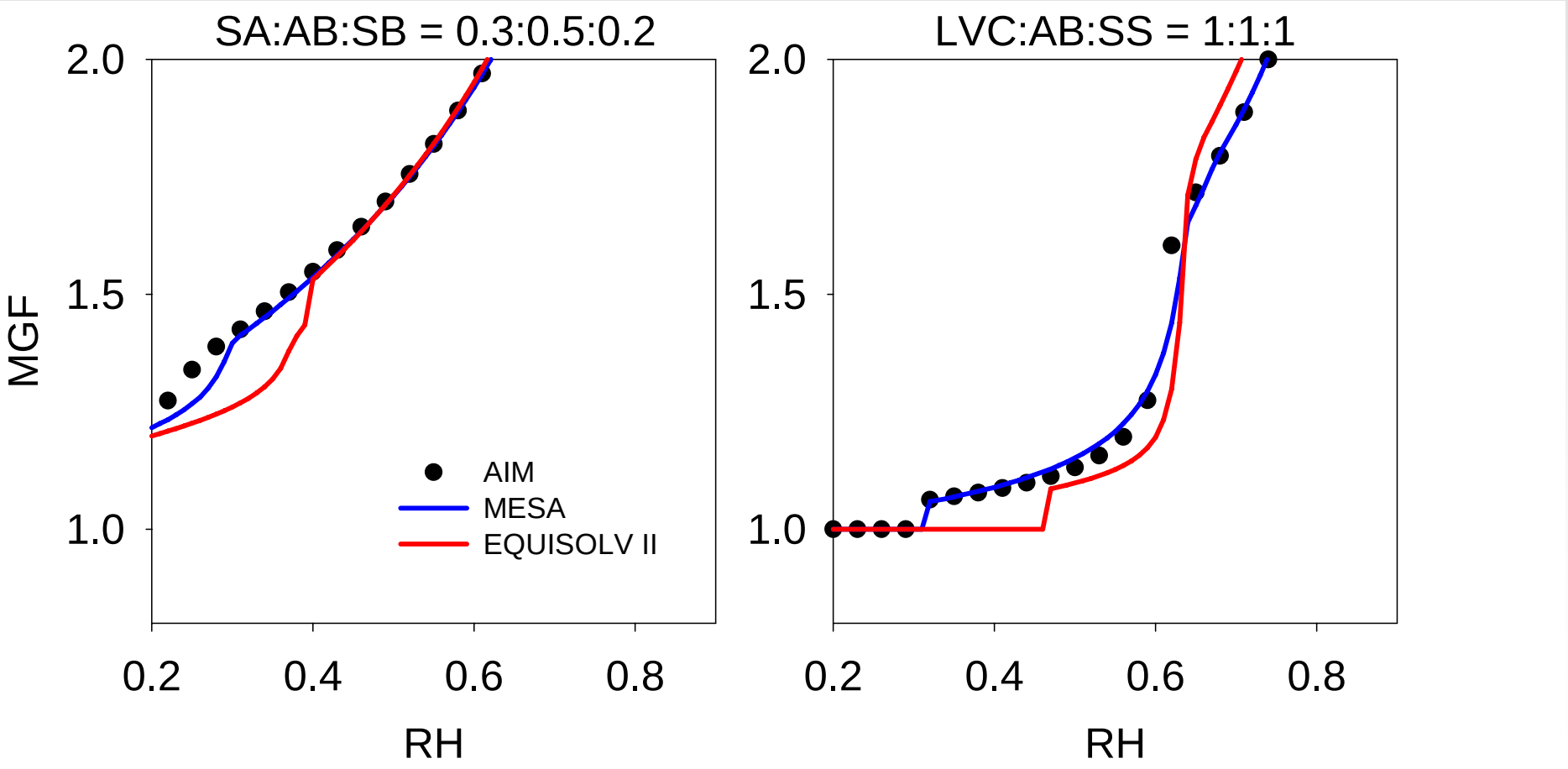
## Sulfate-Poor Test Cases




**Deviations in EQUISOLV II are due to errors in activity coefficients**

# MESA Accuracy Using AIM as Benchmark

## Sulfate-Rich Test Cases




**Deviations in EQUISOLV II are due to errors in activity coefficients**

# MESA: Computational Efficiency

**RMS Relative Convergence Errors**
**MESA = 0.14%  EQUISOLV II = 3.7%**

| 16 Test Cases | |
|---|---|
| **Statistic** | **MESA Speedups Relative to EQUISOLV II** |
| Minimum | **1.7** |
| Maximum | **17.0** |
| Average | **5.8** |

**Platform:** Intel Xeon 3.0 GHz  **Compiler:** Portland Group Fortran 77/90

Because MESA directly predicts MDRH(T), it is ~30 to 40 times faster than EQUISOLV II when RH < MDRH. An important computational advantage at lower temperatures where MDRHs are typically high.

# Dynamic Gas-Particle Partitioning

**Aerosol-Phase**

$$\frac{d[\mathrm{A}]_{i,T,m}}{dt} = k_{i,m}([\mathrm{G}]_i - [\mathrm{G}]^*_{i,m})$$

**Gas-Phase**

$$\frac{d[\mathrm{G}]_i}{dt} = -\sum_m k_{i,m}([\mathrm{G}]_i - [\mathrm{G}]^*_{i,m})$$

$$k_{i,m} = 2\pi \bar{D}_{p,m} N_m F(Kn, \alpha_i) \qquad [\mathrm{s}^{-1}]$$

$i$ = species index

$m$ = aerosol bin index

$D_p$ = aerosol diameter

$N_m$ = aerosol number concentration

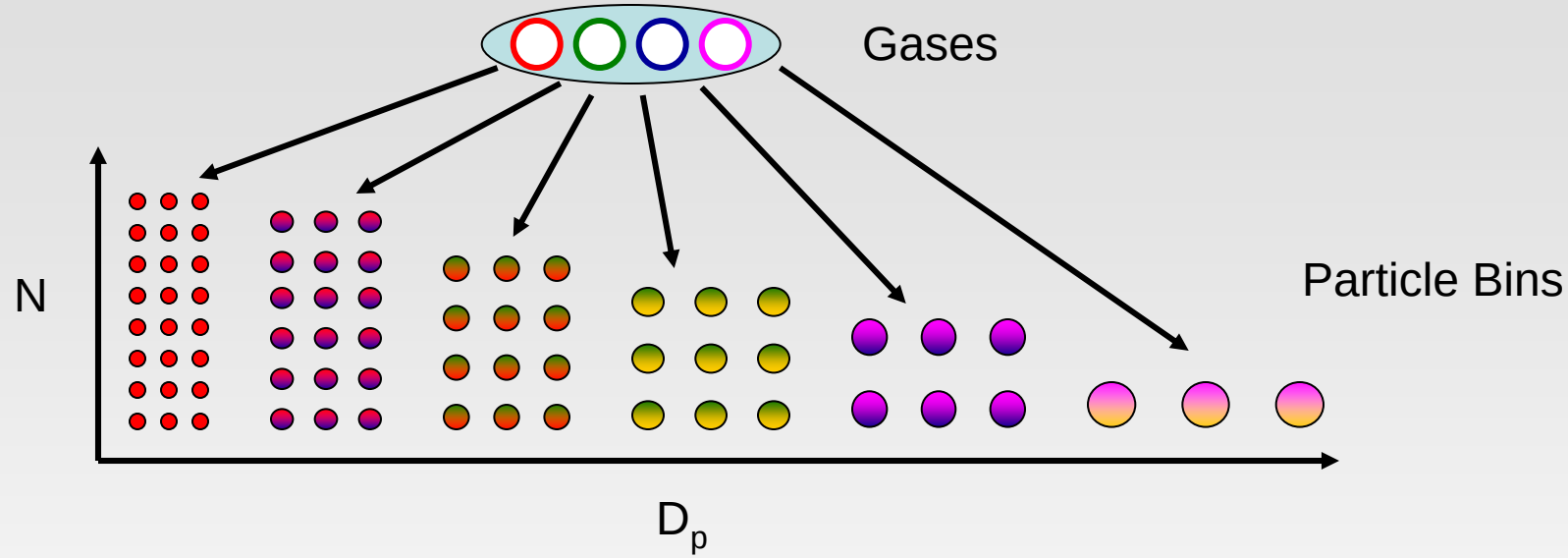
$G^*$ = equilibrium surface concentration

- **Set of implicit non-linear ODEs**
- **Time scales for species/bins may vary over 3 orders of magnitude**
- **Extremely stiff and computationally expensive to solve**

# Gas-Particle Partitioning Solvers

| Model/Solver | Method | Pros and Cons |
|---|---|---|
| SCAPE2 & ISORROPIA | Gas-Liquid-Solid Equilibrium | Efficient but not accurate. Does not give size distribution |
| PNG-EQUISOLV II [Jacobson, 2005] | Fully dynamic using implicit Euler method | Can take long time steps, but prone to unknown errors at low LWC, especially in small particles |
| MADM-Hybrid & MADRID | Combination of equilibrium and dynamic methods | Relatively efficient, but still prone to errors in small particles with equilibrium assumption |
| **ASTEEM** | **Fully dynamic using explicit Euler method** | **Very efficient and accurate for all particle sizes and at all LWCs and RH** |

# **ASTEEM:** Adaptive-step Species Time-split Explicit Euler Method

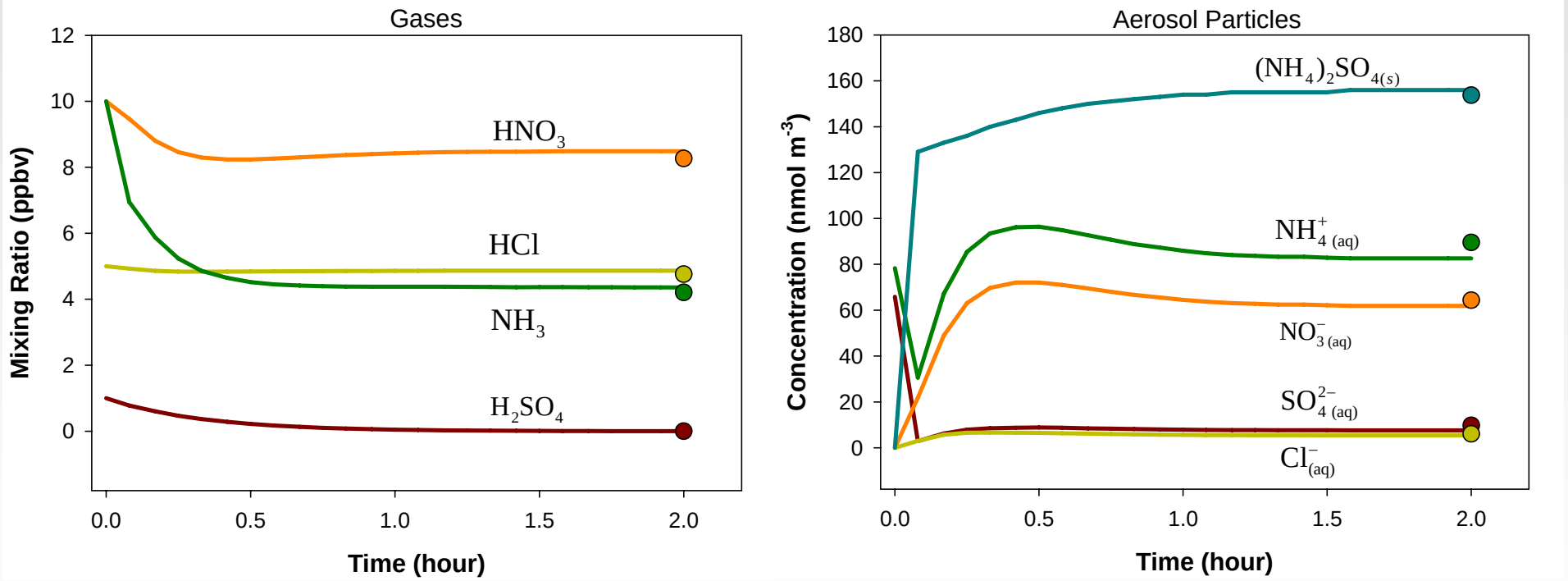



Algorithm:

1. Integrate $H_2SO_4$ and $NH_3$ analytically over all bins for transport time interval, e.g., 5 minutes
2. Compute Time Splitting Interval ($\tau$), e.g., 1 minute, such that gas concentrations don't change more than by ~10%.
3. Solve Solid-Liquid equilibrium with MESA and integrate $HNO_3$, HCl, and $NH_3$ mass transfer over each aerosol bin separately over $\tau$ using an adaptive time stepping scheme.
4. Synchronize all bins at $\tau$ and continue Step 3 until the transport time interval is reached for all bins (5 minutes).

# ASTEEM Accuracy Using AIM as Benchmark

**Single bin: N = 185 $cm^{-3}$, $D_p$ = 0.5 μm, RH = 62%, T = 298 K**

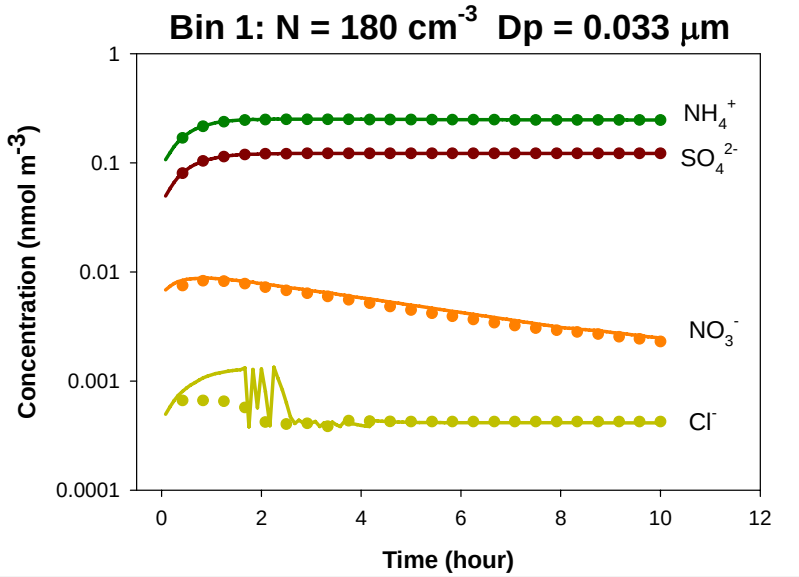


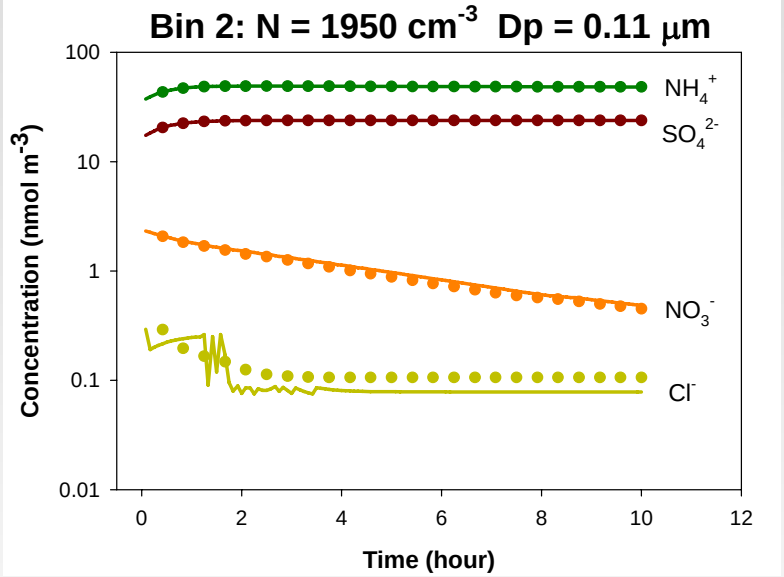

**Lines = MOSAIC (Rigorous dynamic)**

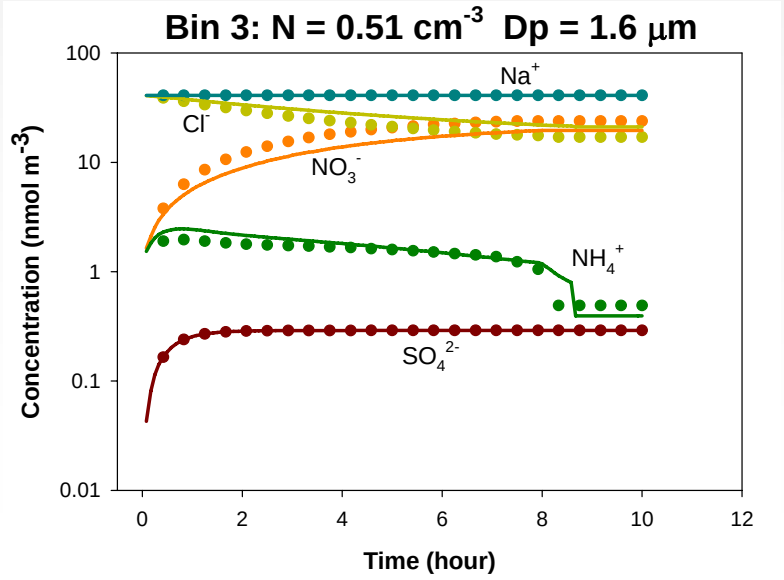
**Circles = AIM (Equilibrium)** [Wexler and Clegg, 2002]

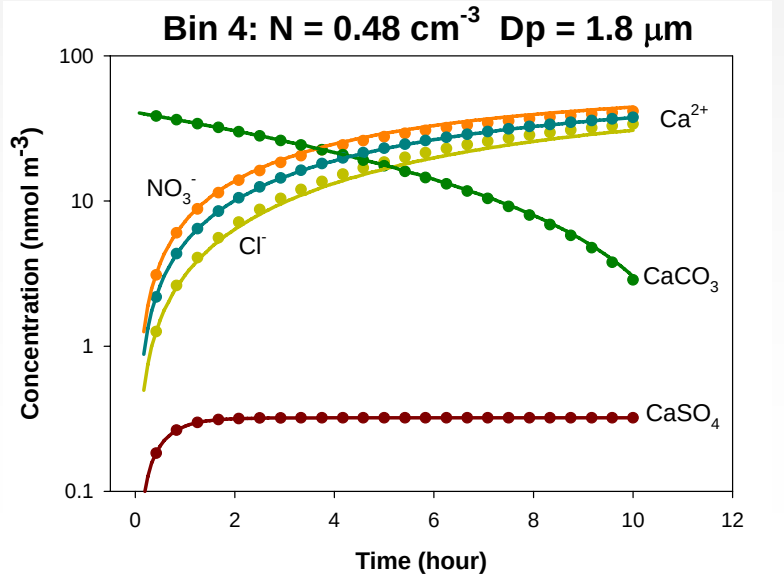
# Multiple Bins:

**Lines = MOSAIC (ASTEEM Dynamic)**
**Circles = MOSAIC (Rigorous Dynamic)**

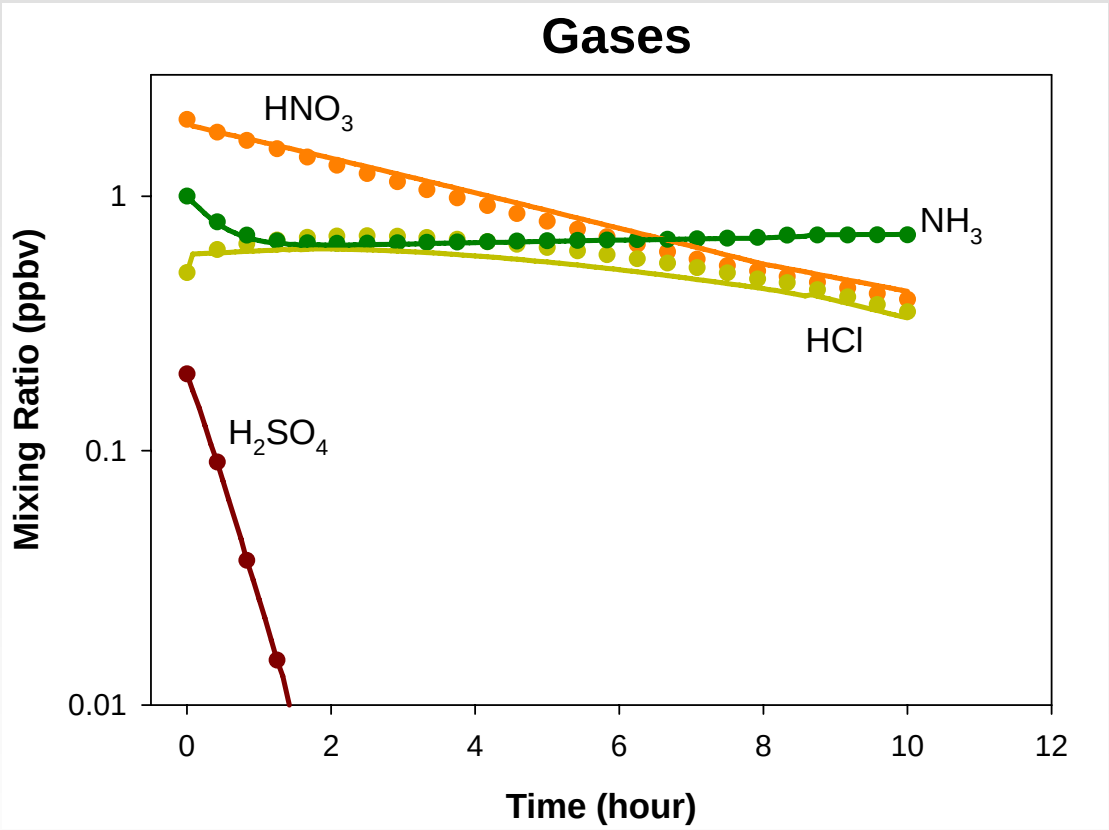


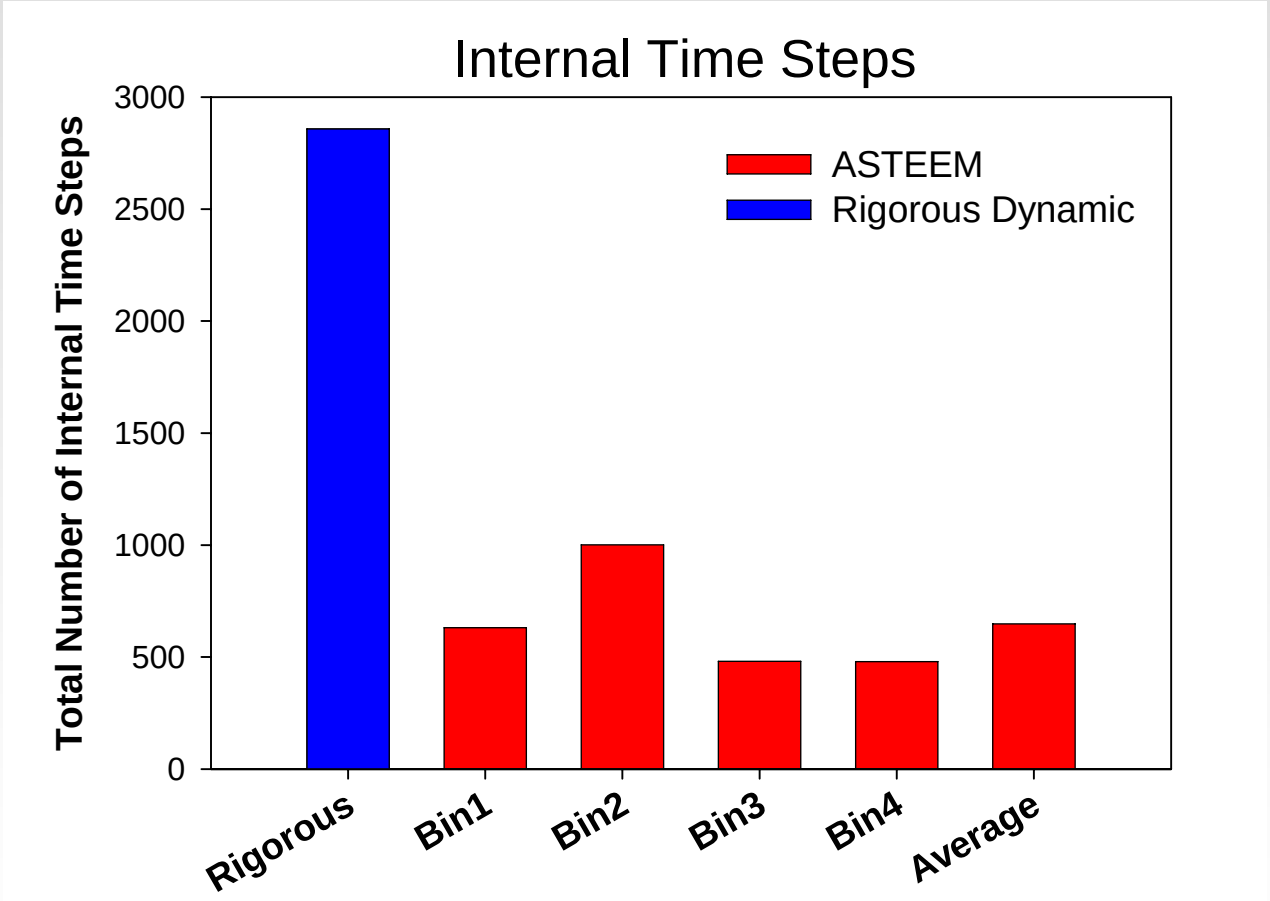



# Gas Phase



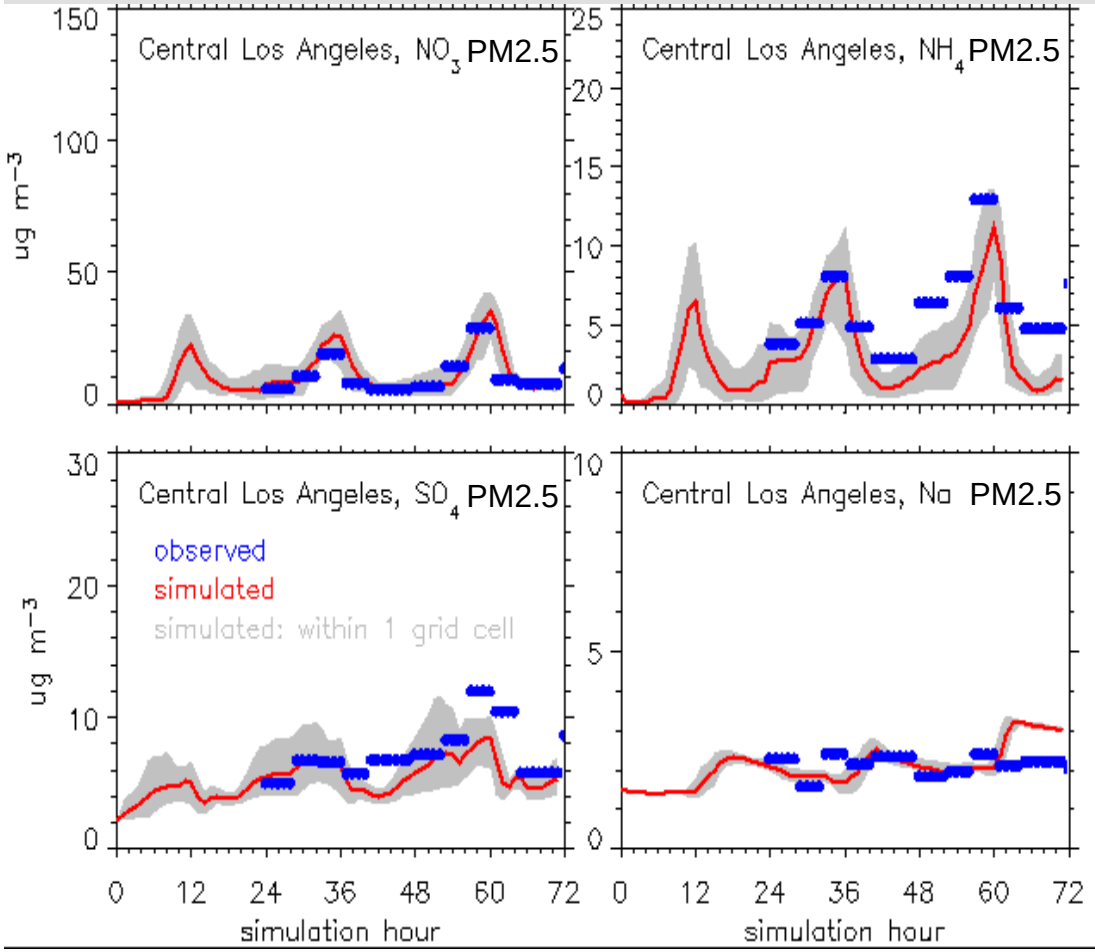

**Lines = MOSAIC (ASTEEM Dynamic)**
**Circles = MOSAIC (Rigorous Dynamic)**

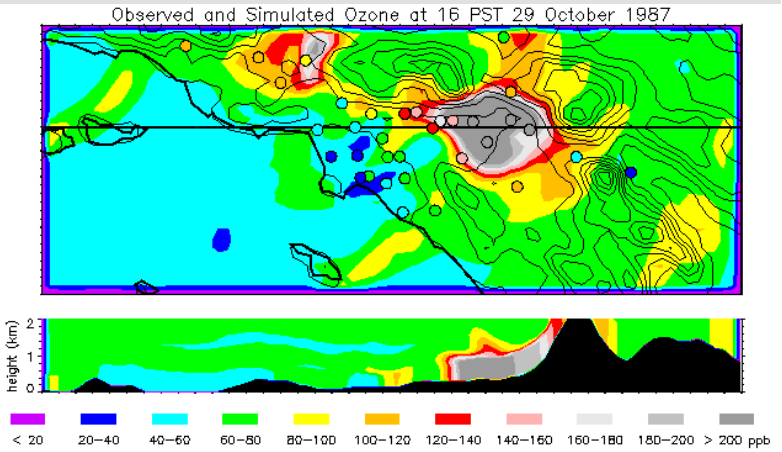
# ASTEEM: Computational Efficiency

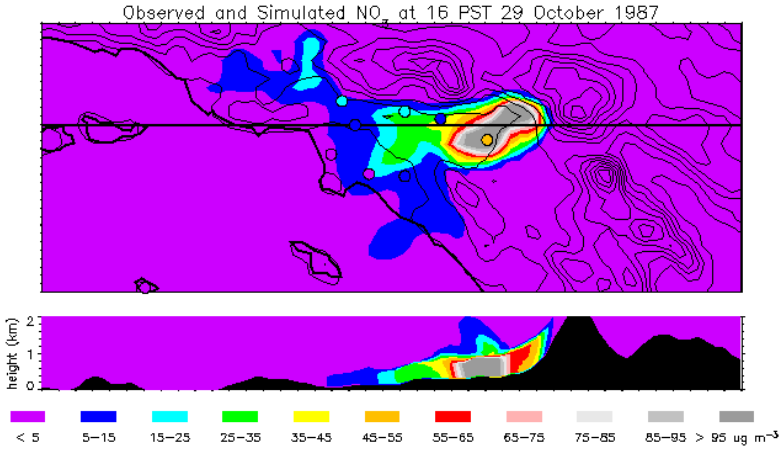



**ASTEEM gives accurate temporal solutions for all aerosol bins with much fewer steps!**

# MOSAIC: Evaluation Using SCAQS 1987 Data




Zaveri R.A., R.C. Easter, J.D. Fast, and L.K. Peters, A new model for simulating aerosol interactions and chemistry (MOSAIC), to be submitted to JGR.

# Summary

- All MOSAIC modules/algorithms are robust, mass conserving, and positive definite.
- Look up tables and simple parameterizations are used where possible for maximum efficiency.
- MOSAIC is more accurate and efficient than other similar modules used in air quality or climate models.
- MOSAIC framework is flexible for both modal and sectional dynamics.
- MOSAIC (and gas-phase mechanism CBM-Z) have been implemented in WRF-Chem.

# Path Forward

- **Add a comprehensive secondary organic aerosol treatment in collaboration with Sasha Madronich.**
- **Work with other ASP PIs to add heterogeneous chemistry, aging processes, and nucleation.**
- **Collaborate with ASP and NSF participants to evaluate comprehensive MOSAIC using field data.**
- **Implement a simplified version in WRF-Chem, and also make it available to regional and global climate modelers.**

# Acknowledgements


- Simon Clegg, University of East Anglia, U.K., for assistance in implementing the PSC model.
- Anthony Wexler, University of California, Davis, for many helpful discussions on various topics in aerosol modeling.
- Mark Z. Jacobson, Stanford University, for his efforts in the intercomparison of MESA and EQUISOLV II.
- Carl Berkowitz, Jerome Fast, Steve Ghan, and Len Peters for their continued support for this work.
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