Aerosol Processes Model Development and Evaluation Plans

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MOSAIC Aerosol Module

Zaveri, R.A., R.C. Easter, J.D. Fast and L.K. Peters, Model for Simulating Aerosol Interactions and Chemistry (MOSAIC), JGR, 113, D13204, 2008.

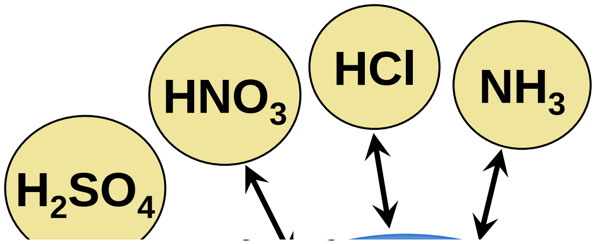
Salient Features

- Treats key aerosol species (SO4, NO3, Cl, CO3, MSA, NH4, Na, Ca, POA, SOA, BC, H2O)
- Sectional and particle-resolved dynamics (*modal version available soon*)
- Fully dynamic gas-particle mass transfer
- Equilibrium particle phase-state and water content
- Heterogeneous chemistry (e.g., N_2O_5 uptake, sea salt and dust aging)
- Robust, accurate, and highly efficient numerics
- Flexible framework for coupling various gas and aerosol processes
- Suitable for 3-D regional and global models
- Implementation in:
  - Weather Research and Forecasting Model (WRF-Chem) – ***done***
  - Global model: Community Atmosphere Model (CAM5) – ***in progress***
  - EPA's CMAQ community model – ***planned***

MOSAIC Components

Process	MOSAIC Sub-Module
Gas-phase Photochemistry	**CBM-Z** **Zaveri and Peters [1999]**
New particle formation (nucleation)	**$H_2SO_4 + H_2O$** **Wexler et al. [1994]**
Coagulation	**Brownian Kernel** **Jacobson et al. [1994]**
Sectional growth	**Two-Moment Method** **Simmel and Wurzler [2006]**
Thermodynamics (activity coefficients)	**MTEM** **Zaveri et al. [2005a]**
Thermodynamics (equilibrium phase state)	**MESA** **Zaveri et al. [2005b]**
Dynamic gas-particle mass transfer (gas-solid, gas-liquid, gas-mixed phase)	**ASTEM** **Zaveri et al. [2008]**
CCN activation parameters	**κ-Köhler** **Petters and Kreidenweis [2007]**
Optical properties	**ACKMIE (Shell-Core)** **Ackerman and Toon [1981]**

Evaluation of Thermod… Transfer Treatments in MOSAIC



Kin… en the gas and size… to 10,000 nm)

No.	Solid-Liquid Equilibrium Reaction
(1)	$(NH_4)_2SO_{4(s)} \rightleftharpoons 2NH^+_{4(aq)} + SO^{2-}_{4(aq)}$
(2)	$NH_4NO_{3(s)} \rightleftharpoons NH^+_{4(aq)} + NO^-_{3(aq)}$
(3)	$NH_4Cl_{(s)} \rightleftharpoons NH^+_{4(aq)} + Cl^-_{(aq)}$
(4)	$Na_2SO_{4(s)} \rightleftharpoons 2Na^+_{(aq)} + SO^{2-}_{4(aq)}$
(5)	$NaNO_{3(s)} \rightleftharpoons Na^+_{(aq)} + NO^-_{3(aq)}$
(6)	$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$
(7)	$Ca(NO_3)_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2NO^-_{3(aq)}$
(8)	$CaCl_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2Cl^-_{(aq)}$
(9)	$(NH_4)_3H(SO_4)_{2(s)} \rightleftharpoons 3NH^+_{4(aq)} + HSO^-_{4(aq)} + SO^{2-}_{4(aq)}$
(10)	$NH_4\ HSO_{4(s)} \rightleftharpoons NH^+_{4(aq)} + HSO^-_{4(aq)}$
(11)	$NaHSO_{4(s)} \rightleftharpoons Na^+_{(aq)} + HSO^-_{4(aq)}$
(12)	$HSO_{4(aq)}^- \rightleftharpoons H^+_{(aq)} + SO^{2-}_{4(aq)}$

No.	Reversible Gas-Particle Reactions
	gas-solid
(E1)	$NH_4Cl(s) \leftrightarrow NH_3(g) + HCl(g)$
(E2)	$NH_4NO_3(s) \leftrightarrow NH_3(g) + HNO_3(g)$
	gas-liquid
(E3)	$NH_3(g) \leftrightarrow NH_3(aq)$
(E4)	$HNO_3(g) \leftrightarrow H^+(aq) + NO_3^-(aq)$
(E5)	$HCl(g) \leftrightarrow H^+(aq) + Cl^-(aq)$
	liquid-liquid
(E6)	$H_2O(aq) + NH_3(aq) \leftrightarrow OH^-(aq) + NH_4^+(aq)$
(E7)	$H_2O(aq) \leftrightarrow H^+(aq) + OH^-(aq)$
(E8)	$HSO_4^-(aq) \leftrightarrow H^+(aq) + SO_4^{2-}(aq)$

No.	Irreversible Heterogeneous Reactions
	Reactions With $H_2SO_4(g)$
(R1)	$CaCO_3(s) + H_2SO_4(g) \rightarrow CaSO_4(s) + H_2O(g)\uparrow + CO_2(g)\uparrow$
(R2)	$CaCl_2(s,l) + H_2SO_4(g) \rightarrow CaSO_4(s) + 2HCl(g)\uparrow$
(R3)	$Ca(NO_3)_2(s,l) + H_2SO_4(g) \rightarrow CaSO_4(s) + 2HNO_3(g)\uparrow$
(R4)	$2NaCl(s,l) + H_2SO_4(g) \rightarrow Na_2SO_4(s,l) + 2HCl(g)\uparrow$
(R5)	$2NaNO_3(s,l) + H_2SO_4(g) \rightarrow Na_2SO_4(s,l) + 2HNO_3(g)\uparrow$
(R6)	$(CH_3SO_3)_2Ca(s,l) + H_2SO_4(g) \rightarrow CaSO_4(s) + 2CH_3SO_3H(l)$
	Reactions With $CH_3SO_3H(g)$
(R7)	$CaCO_3(s) + 2CH_3SO_3H(g) \rightarrow (CH_3SO_3)_2Ca(s,l) + H_2O(g)\uparrow + CO_2(g)\uparrow$
(R8)	$CaCl_2(s,l) + 2CH_3SO_3H(g) \rightarrow (CH_3SO_3)_2Ca(s,l) + 2HCl(g)\uparrow$
(R9)	$Ca(NO_3)_2(s,l) + 2CH_3SO_3H(g) \rightarrow (CH_3SO_3)_2Ca(s,l) + 2HNO_3(g)\uparrow$
(R10)	$NaCl(s,l) + CH_3SO_3H(g) \rightarrow CH_3SO_3Na(s,l) + HCl(g)\uparrow$
(R11)	$NaNO_3(s,l) + CH_3SO_3H(g) \rightarrow CH_3SO_3Na(s,l) + HNO_3(g)\uparrow$
	Reactions With $HNO_3(g)$
(R12)	$CaCO_3(s) + 2HNO_3(g) \rightarrow Ca(NO_3)_2(s) + H_2O(g)\uparrow + CO_2(g)\uparrow$
(R13)	$CaCl_2(s) + 2HNO_3(g) \rightarrow Ca(NO_3)_2(s) + 2HCl(g)\uparrow$
(R14)	$NaCl(s) + HNO_3(g) \rightarrow NaNO_3(s) + HCl(g)\uparrow$
	Reactions With $HCl(g)$
(R15)	$CaCO_3(s) + 2HCl(g) \rightarrow CaCl_2(s) + H_2O(g)\uparrow + CO_2(g)\uparrow$
	Reactions With $NH_3(g)$
(R16)	$NH_4HSO_4(s) + NH_3(g) \rightarrow (NH_4)_2SO_4(s)$
(R17)	$(NH_4)_3H(SO_4)_2(s) + NH_3(g) \rightarrow 2(NH_4)_2SO_4(s)$
(R18)	$2NaHSO_4(s) + NH_3(g) \rightarrow Na_2SO_4(s) + NH_4HSO_4(s)$

- **These processes together pose an extremely stiff ODE problem.**
- **Numerically difficult and expensive to solve!**

ORY

Aerosol Processes of Current Interest

- Secondary organic aerosol (SOA) formation
- Thermodynamic properties of mixed organic-inorganic particles
- Growth of newly formed particles to CCN active sizes
- Evolution of black carbon (BC) mixing state
- Effect of mixing state and organics on optical and CCN activation properties

Secondary Organic Aerosol

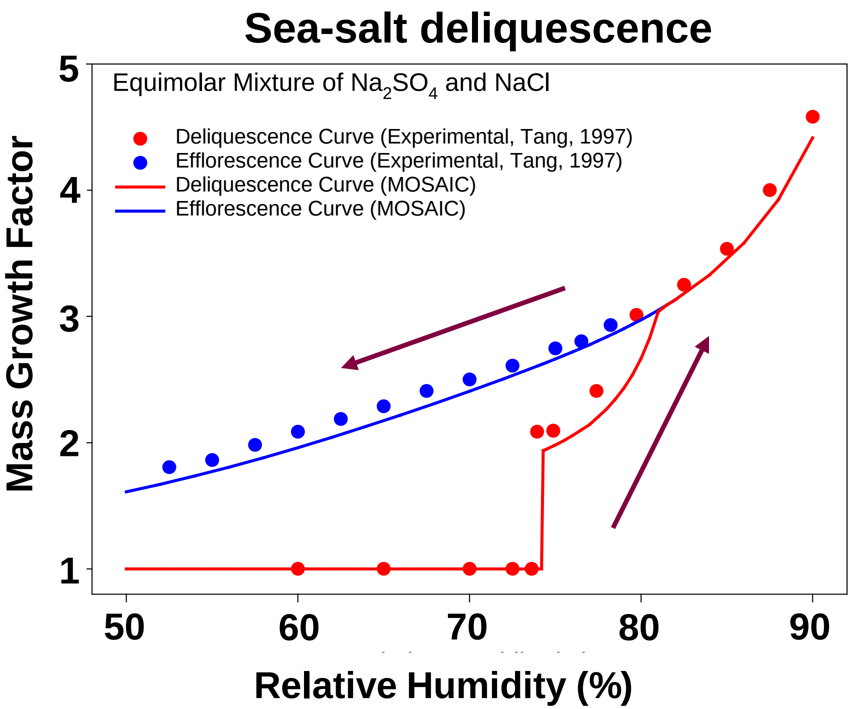
- Sasha Madronich and colleagues have developed the explicit chemical mechanism **GECKO-A** (Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere)

- Map GECKO-A output on a polarity-vapor pressure grid proposed by J. Pankow and K. Barsanti

- Develop and implement a condensed version of GECKO-A in MOSAIC

Aerosol Thermodynamics

- Mutual deliquescence point
- Solid-liquid equilibrium
- Equilibrium water content
- Water hysteresis



A good treatment for phase-state is needed for moderate to low RH values since it determines the particle size and composition, which have a profound effect on the aerosol optical properties

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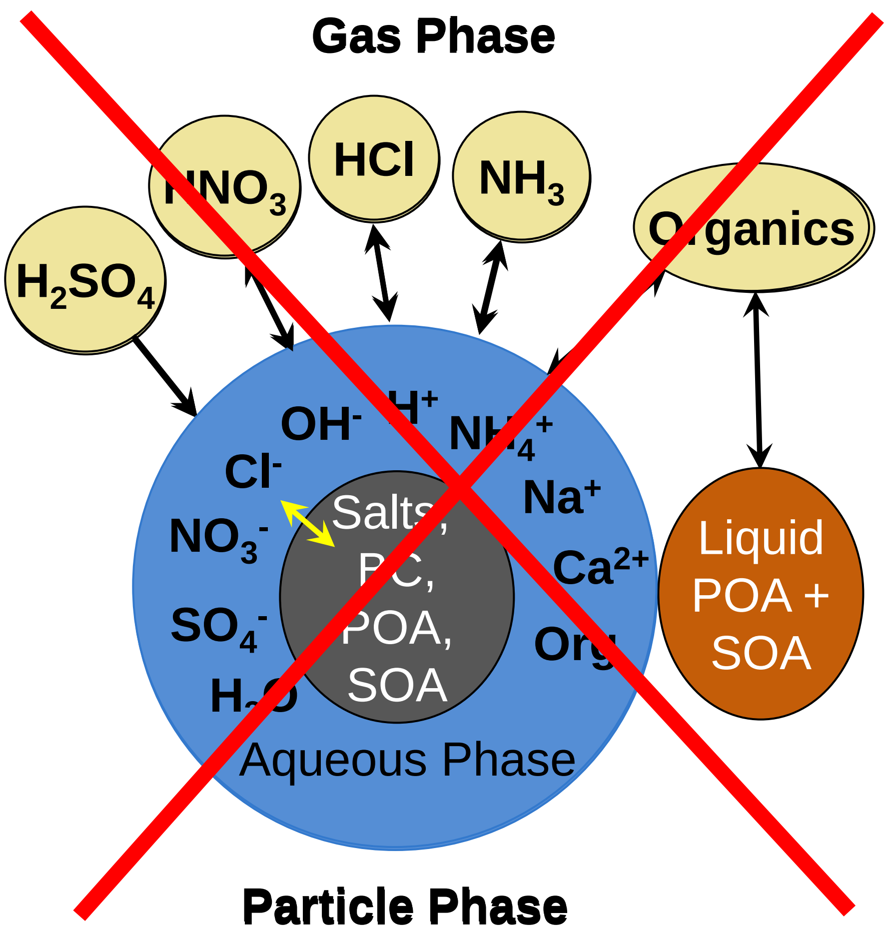
Interactions between Inorganics and Organics

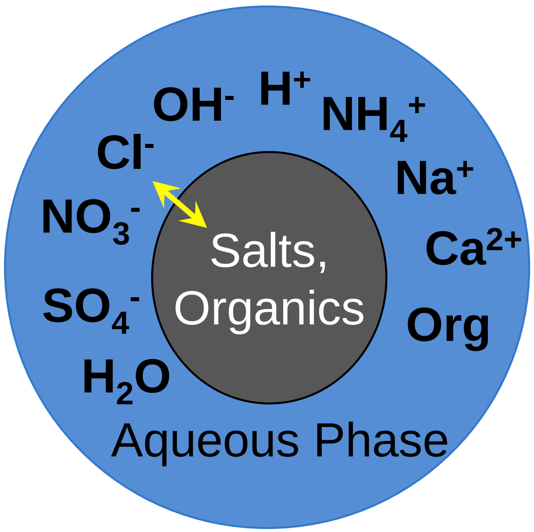


Evidence of the effect of organics

- Saxena et al., Organics alter hygroscopic behaviour of atmospheric particles, JGR, 1995.
- Choi, M. Y. and Chan, C. K.: The Effects of Organic Species on the Hygroscopic Behaviors of Inorganic Aerosols, ES&T, 2002.
- Gysel et al., Hygroscopic properties of water-soluble matter and humic-like organics in atmospheric fine aerosol, ACP, 2004.
- Marcolli and Krieger, Phase changes during hygroscopic cycles of mixed organic/inorganic model systems of tropospheric aerosols, JPCA, 2006.
- Virtanen et al., An amorphous solid state of biogenic secondary organic aerosol particles, Nature, 2010.

Interactions between Inorganics and Organics

Modified Phase-State and Aerosol Water Content Determination



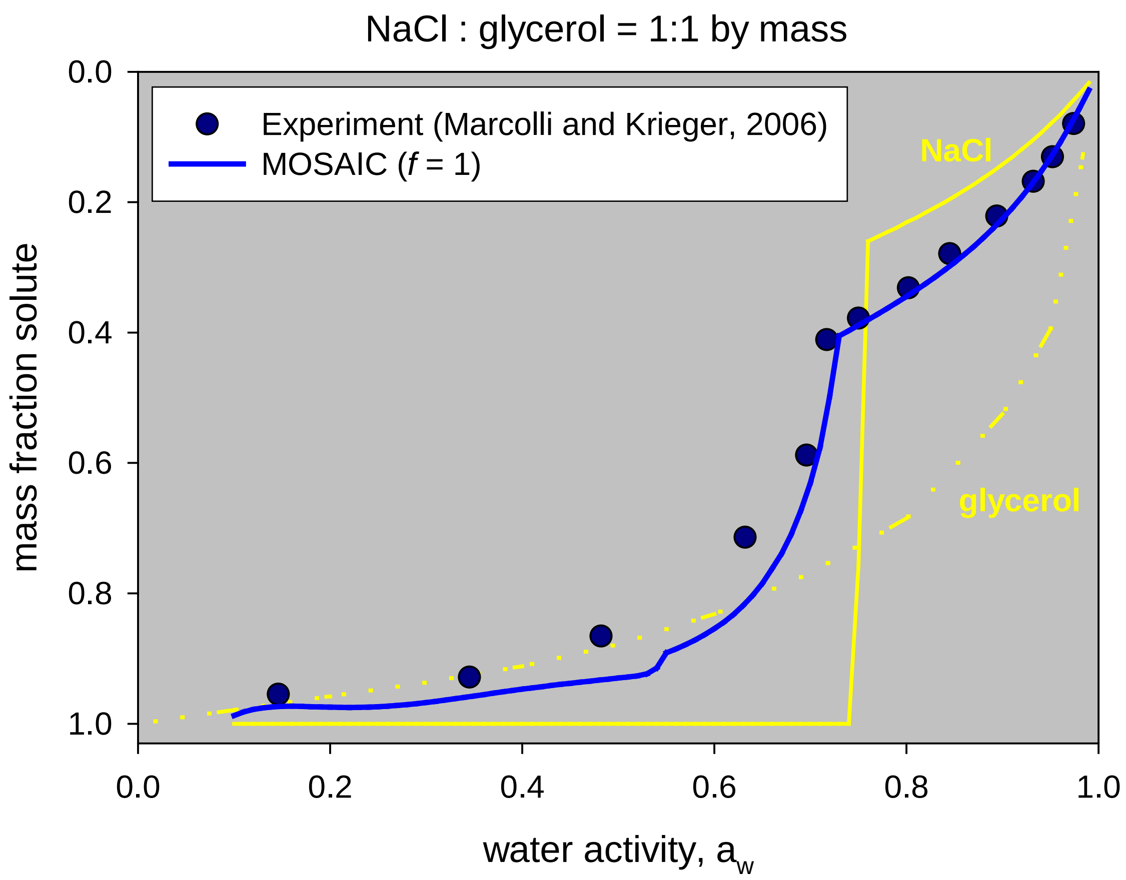
$$W_{total} = W_{inorganics} + W_{organics}$$

$$W_{total} = \underbrace{W_{inorganics} + f\,W_{organics}}_{\text{}} + \underbrace{(1-f)W_{organics}}_{\text{}}$$

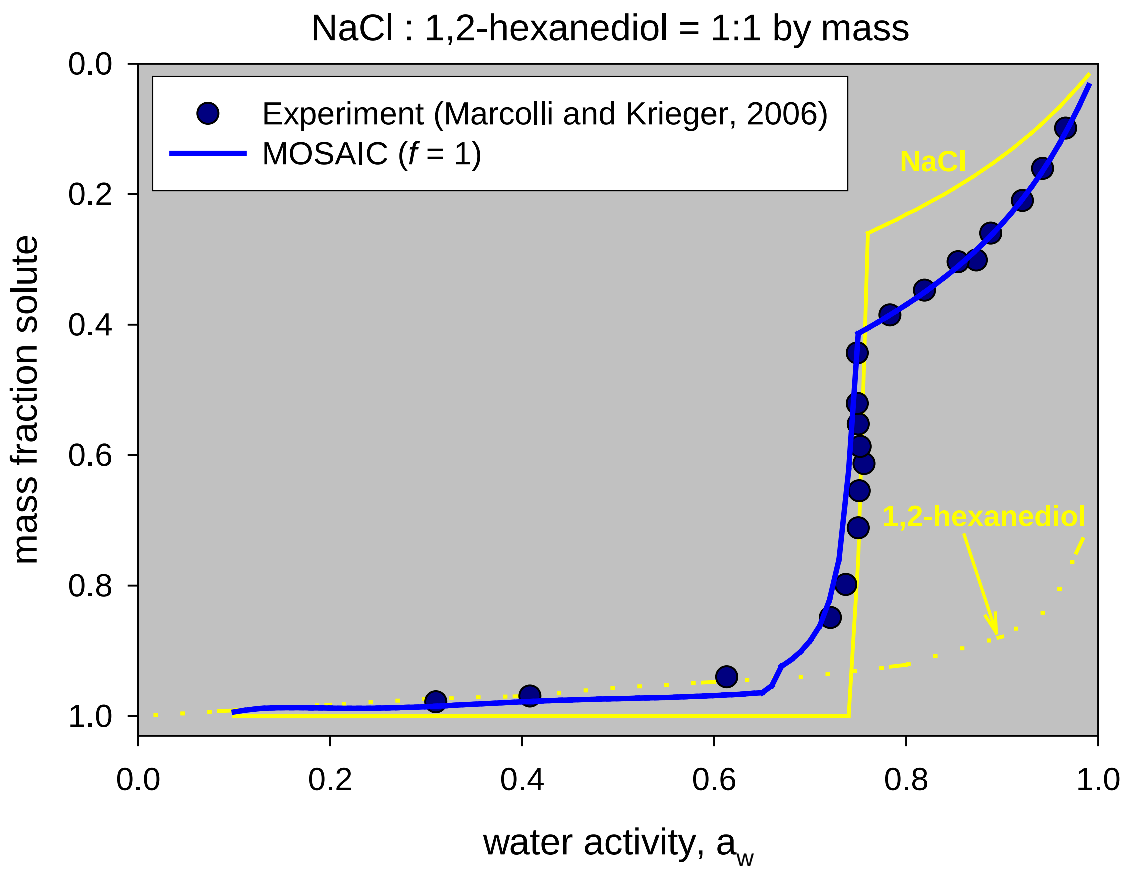
Water shared between inorganics and organics, which is used to dissolve inorganics in phase-state calculations

Water due to organics that is NOT available to dissolve inorganics

NaCl + Glycerol



NaCl + 1,4-hexanediol



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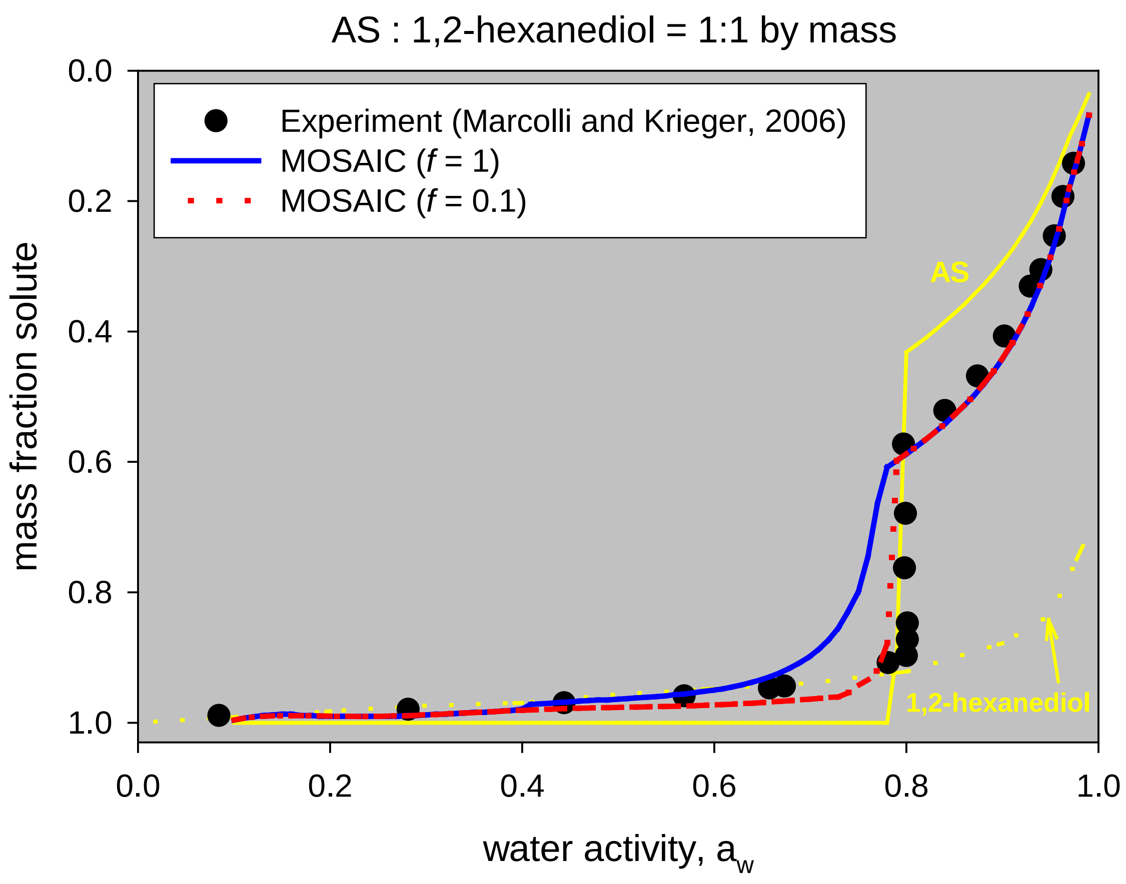
Ammonium Sulfate + 1,2-hexanediol



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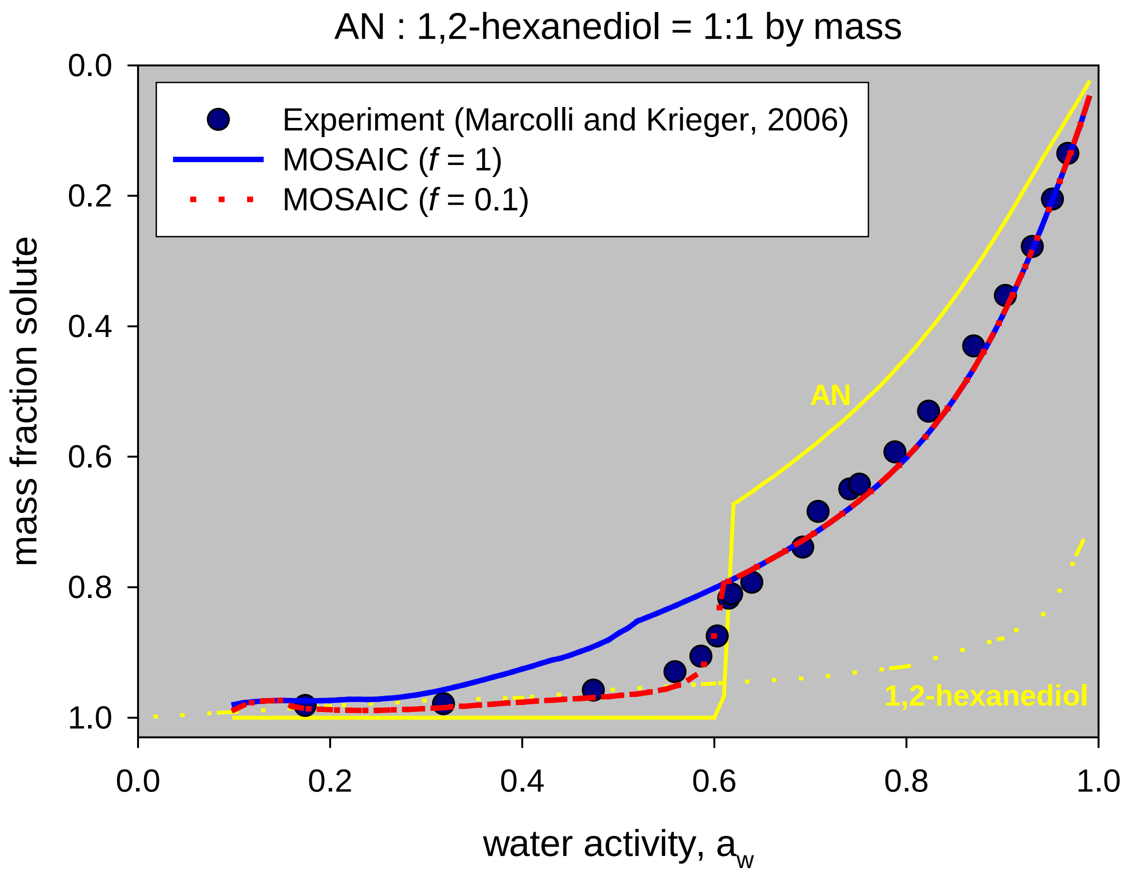
Ammonium Nitrate + 1,2-hexanediol



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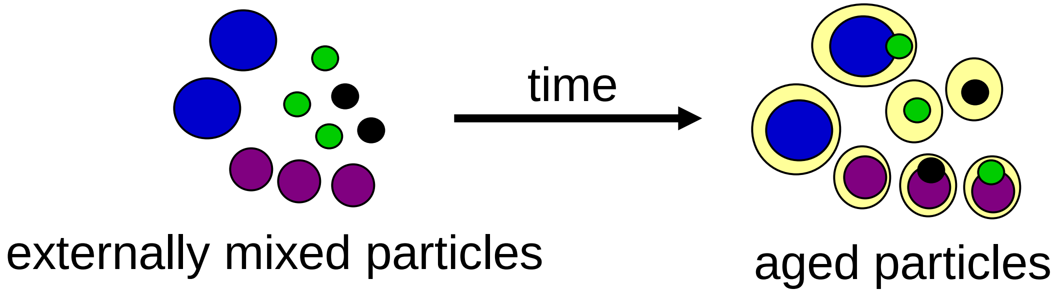
Comprehensive Treatment Needed

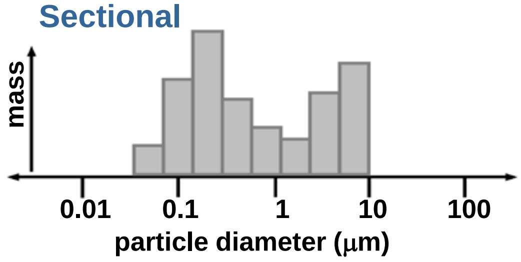
- Need growth data for authentic SOA + inorganic mixtures
  - Biogenic SOA + inorganic mixtures
  - Anthropogenic SOA + inorganic mixtures
- Develop and evaluate the *f-factor* parameterization
  - Parameter *f* as a function of O:C ratio, OOA, HOA, BBOA, morphology, etc.
  - Evaluate using field observations (AMS, SPLAT, HTDMA)

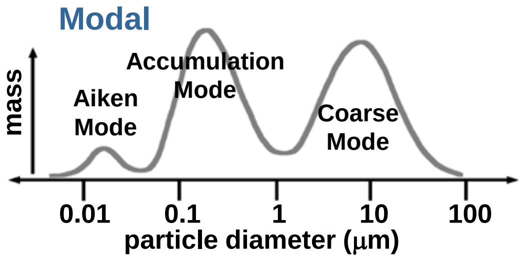
Aerosol Mixing State Evolution

- Mixing-states of primary aerosols change over time by coagulation, condensation, emission, dilution, and other processes.



- Aerosol mixing-state affects optical properties, CCN activation properties, and ice nucleation properties
- Traditional sectional and modal aerosol models do not adequately resolve aerosol mixing state





Particle-Resolved Modeling Approach

Extended MOSAIC to a particle-resolved aerosol framework to explicitly simulate evolution of particle number, mass, and mixing-state

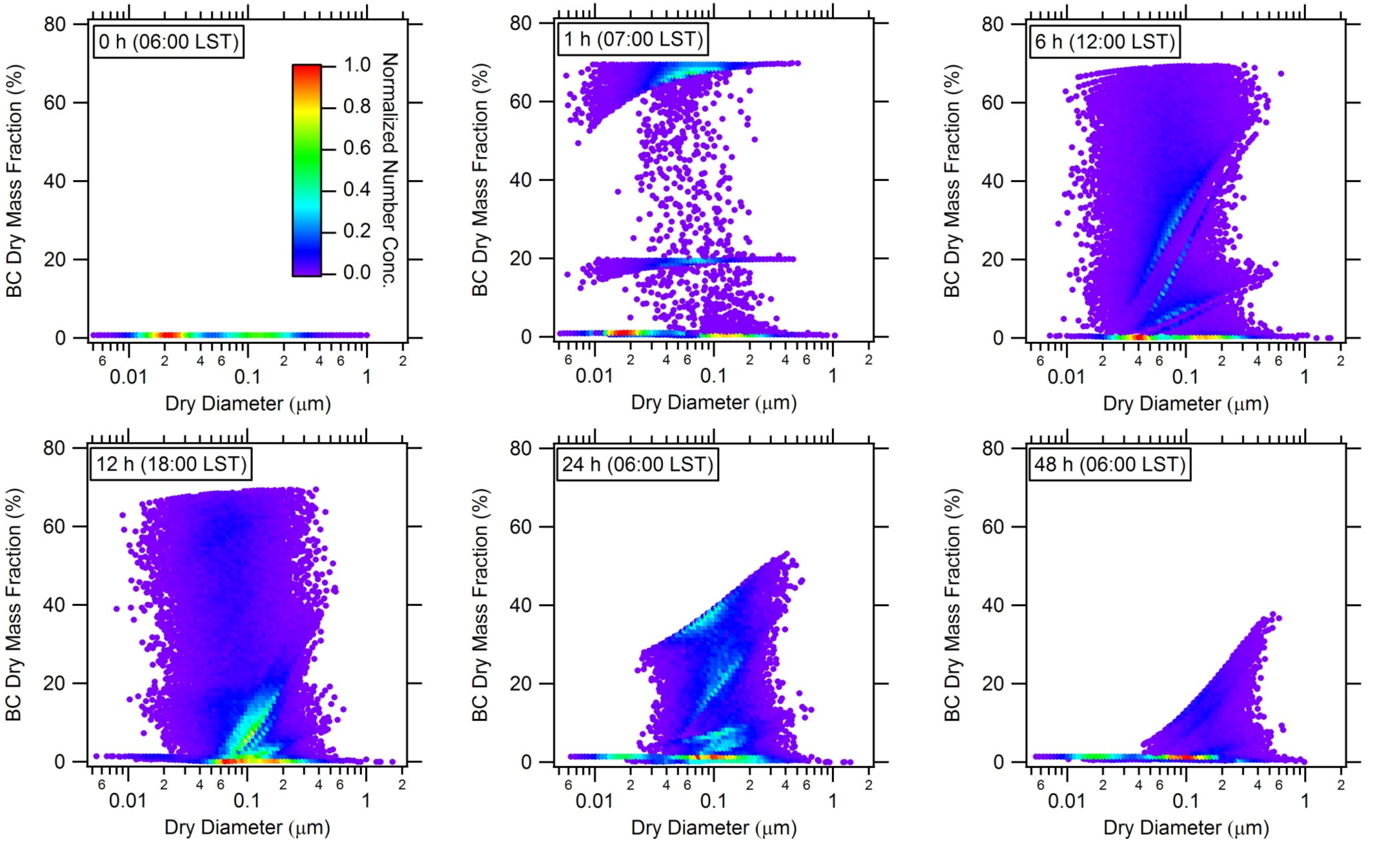
- Explicitly resolve individual particles in a complex aerosol within a small volume of air that represents a much larger well-mixed air mass of interest

- Use MOSAIC modules for trace gas emission, dilution, photochemistry, aerosol thermodynamics, and gas-particle mass transfer

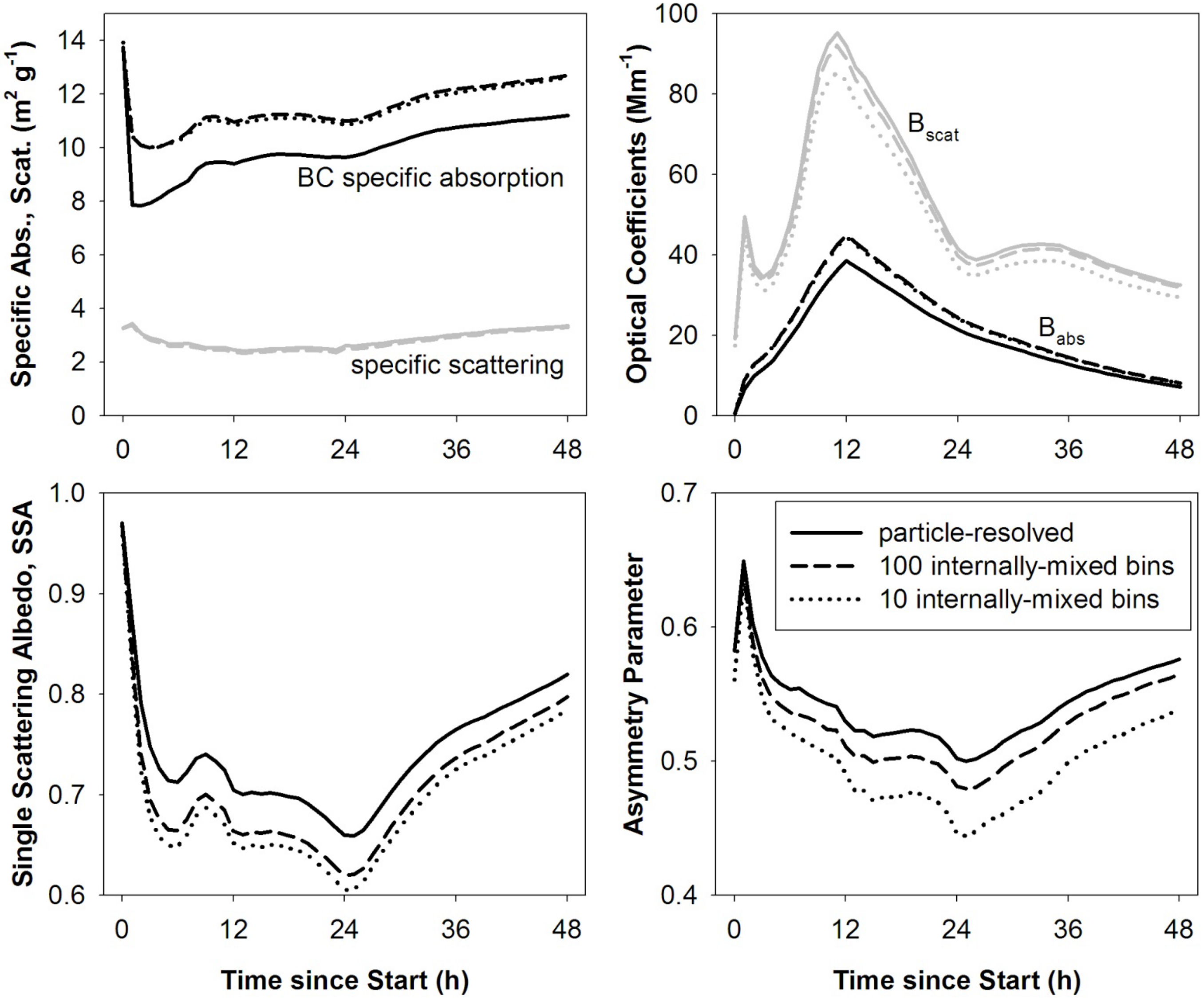
- Use PartMC, a stochastic Monte Carlo module, for particle coagulation, emission, and dilution

PartMC-MOSAIC serves as a numerical benchmark for evaluating sectional and modal approaches used in 3-D models

Sample Result: Particle-Resolved Evolution of Aerosol Mixing State in an Urban Plume

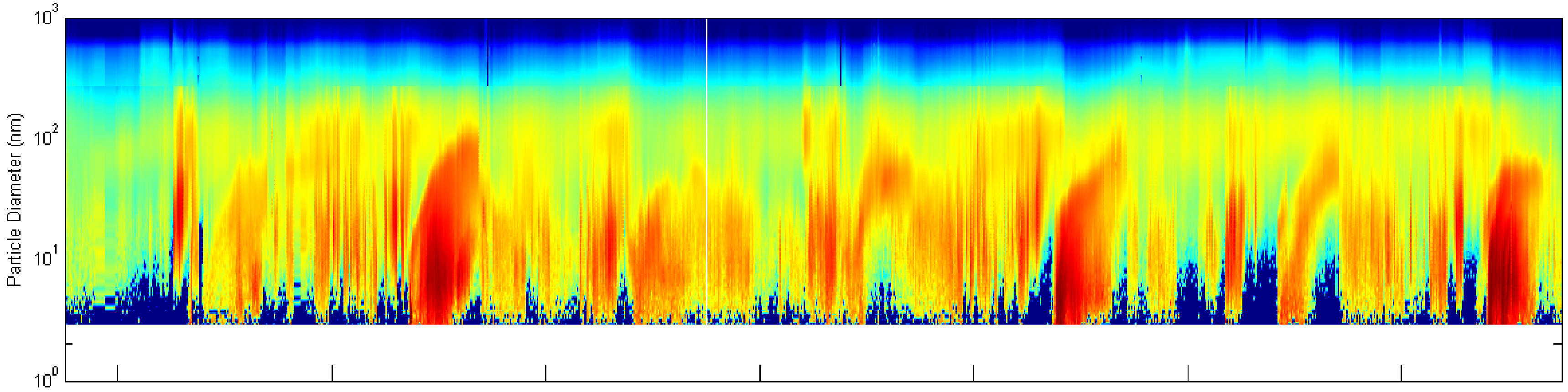


Effect of Binning on Ensemble Mean Optical Properties



Nucleation and Growth in an Urban Air Mass

Observations of nucleation and growth during MILAGRO 2006

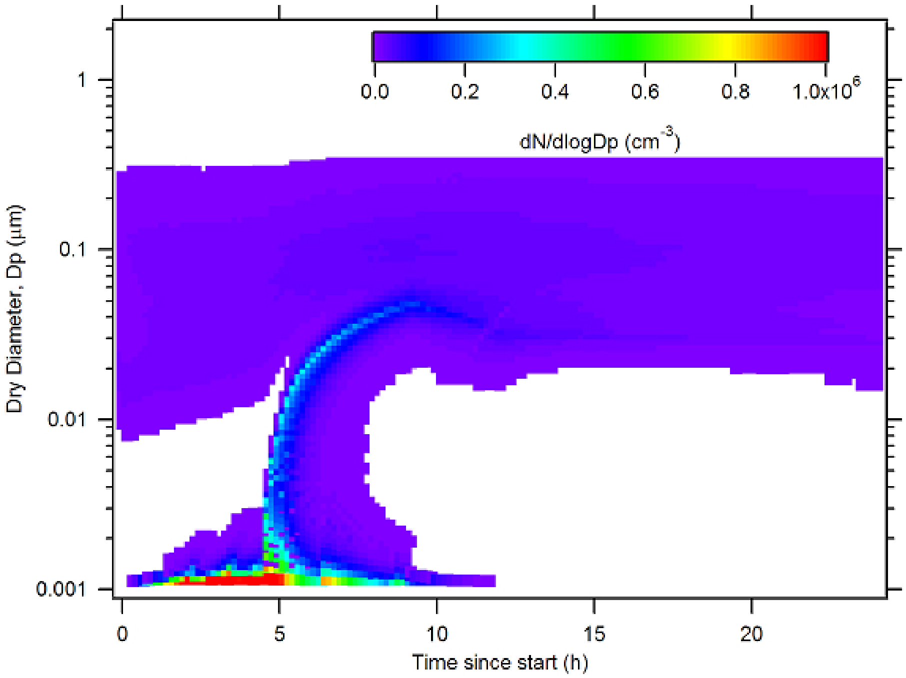


Examine the Role of Ammonium Nitrate in the Growth of Nanoparticles

- **Ammonium nitrate is semi-volatile and very tricky to simulate**
- **Formation depends on**
  - **Gas-phase concentrations of HNO_3 and NH_3**
  - **Particle-phase composition (esp., acidity) and phase state**
  - **Temperature and relative humidity**

Modeled Growth of Newly Formed Particles

RH = 40%



Rapid growth due to NH_4NO_3 condensation on dry particles

WRONG REASON!

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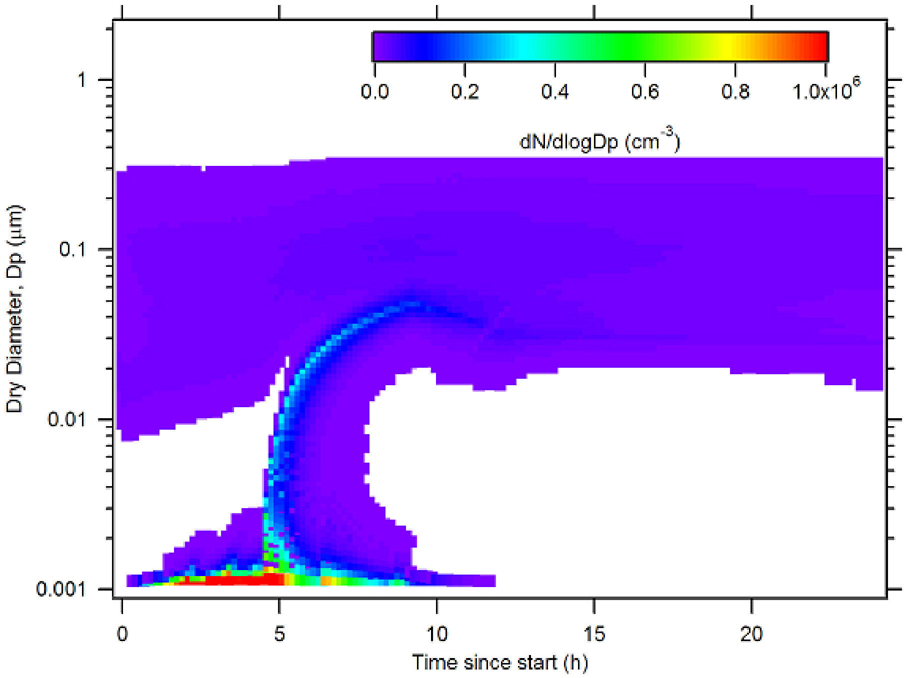
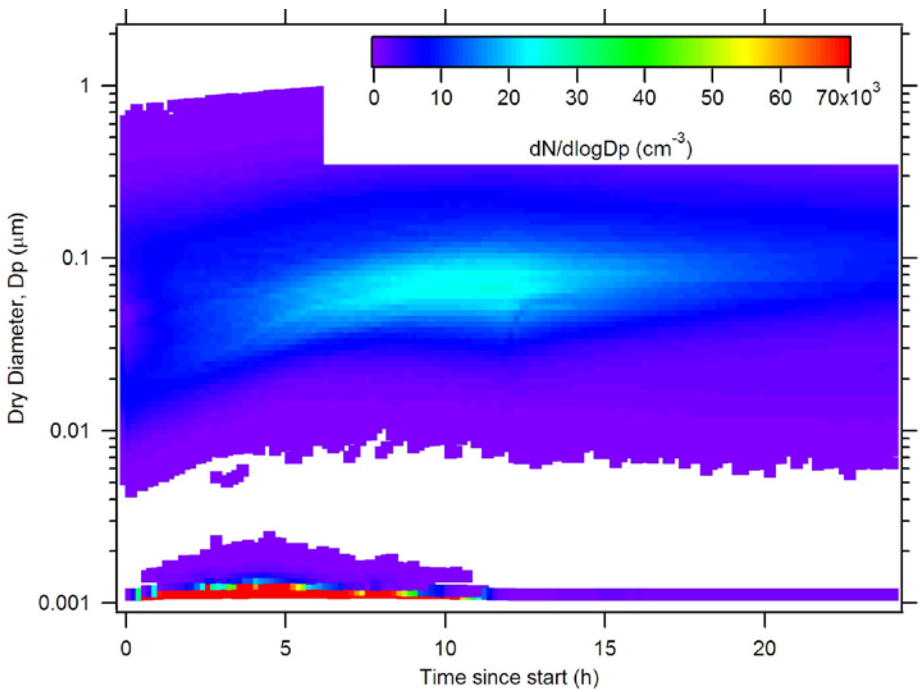
Growth of Newly Formed Particles

RH = 40%



Rapid growth due to NH_4NO_3 condensation on dry particles

RH = 85%



No growth due to strong Kelvin effect

Model Evaluation Using CARES Data

- Local closures for optical and CCN activation properties
- Constrained Lagrangian modeling for CARES episodes
  - SOA formation
  - BC mixing state evolution
- Constrained modeling of growth of newly formed particles to CCN active sizes