Modeling Dynamic Partitioning of Semi-volatile Organic Gases to Size-Distributed Aerosols

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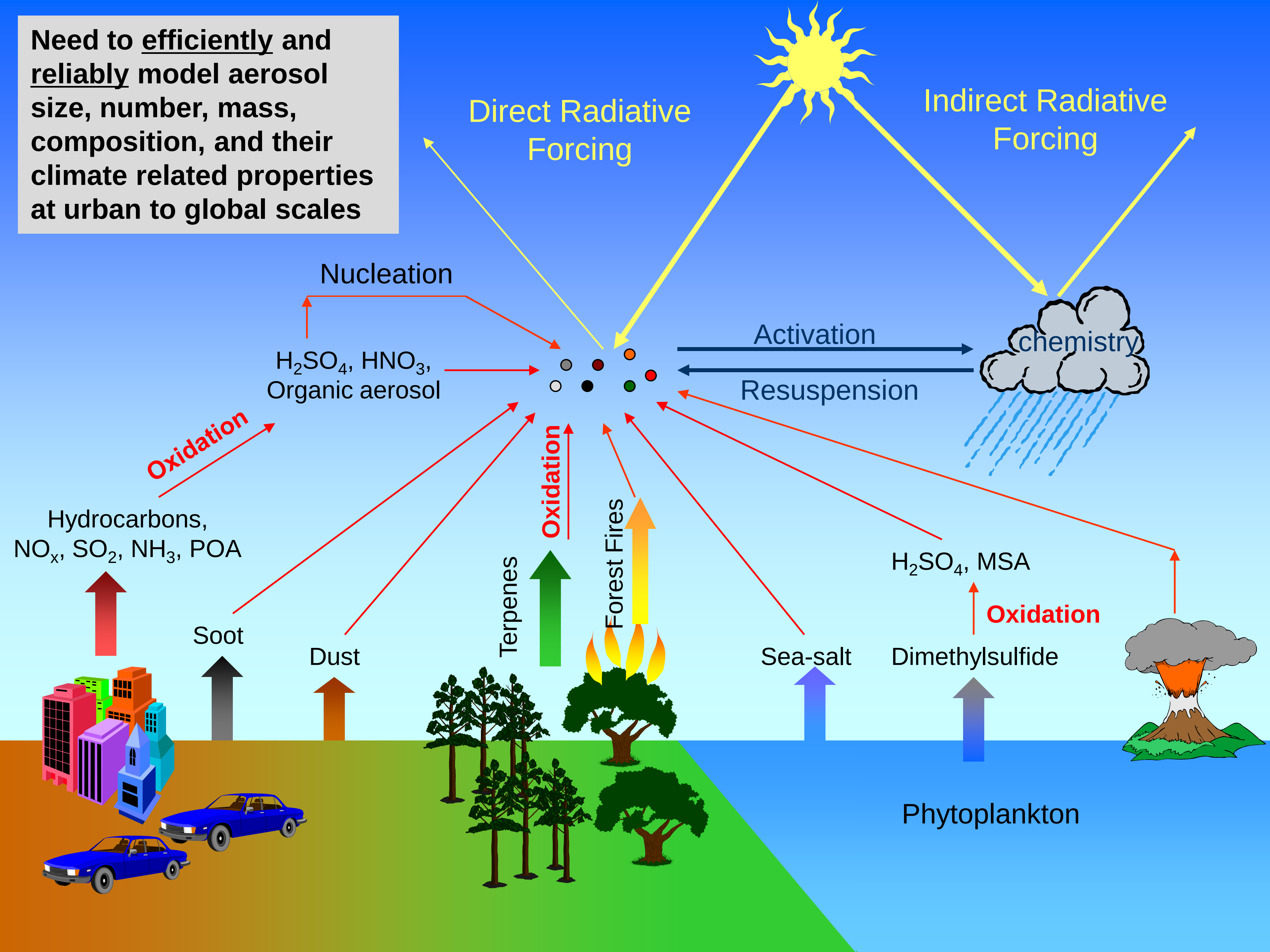
Outline

- **Motivation**
- **SOA formation processes**
- **SOA modeling challenges**
- **MOSAIC aerosol modeling framework**
- **Gas-particle partitioning of organic gases (*new*)**
- **Sample results**
- **Future Directions**


Need to efficiently and reliably model aerosol size, number, mass, composition, and their climate related properties at urban to global scales
Direct Radiative Forcing
Indirect Radiative Forcing
Nucleation
H_2SO_4, HNO_3, Organic aerosol
Activation
Resuspension
chemistry
Oxidation
Hydrocarbons, NO_x, SO_2, NH_3, POA
Soot
Dust
Terpenes
Oxidation
Forest Fires
Sea-salt
H_2SO_4, MSA
Oxidation
Dimethylsulfide
Phytoplankton

SOA Formation Processes

- Up to 90% of submicron aerosol mass is composed of organics (Kanakidou et al., 2005; Zhang et al., 2007)
- SOA formation is quite rapid (within a few hours) during daytime (Volkamer et al., 2006; Kleinman et al., 2007; de Gouw et al., 2008)
- SOA from oxidation of SVOCs from diesel exhaust may help explain some of the missing organic aerosol mass in models (Robinson et al., 2007)
- Observed rapid growth of newly formed particles (via homogeneous nucleation) is thought to be by SOA condensation (Kuang et al., 2008)
- Anthropogenic and biogenic SOA precursors may interact to enhance the overall SOA yield (Weber et al., 2007)
- Particle-phase reactions of absorbed VOCs within inorganic particles can form SOA (Jang et al., 2003; Kroll et al., 2005; Liggio et al., 2005)
- Accretion reactions, including aldol condensation, acid dehydration, and gem-diol condensation can transform VOCs into oligomeric compounds (Gao et al., 2004; Jang et al., 2003; Kalberer et al., 2004)

SOA Modeling Challenges

- Gas-particle partitioning processes are still poorly understood at a fundamental level
- How do we handle the complexities in the gas-phase VOC chemistry?
- Should we use Raoult's Law or some sort of reactive uptake formulation as driving force for gas-particle mass transfer?
- Should we use Henry's Law if the organics are dissolved in the aqueous phase?
- Are the organic particles liquid or solid? Virtanen et al. (2011) and Vaden et al. (2011) suggest that SOA particles are solid.
- How do we treat organic-inorganic interactions and the associated phase transitions?
- How do we treat particle-phase reactions? What are the time scales?
- What are the anthropogenic-biogenic interactions? How do we reliably represent them in models?

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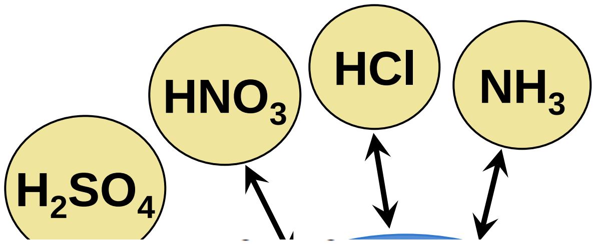
General Problem Solving Approach

- Develop a comprehensive aerosol model framework that includes all the processes that we think are (or might be) important
- Evaluate the roles of specific processes using appropriate laboratory and field observations
- Simplify, parameterize, and optimize the process model as much as possible to increase computational efficiency and decrease memory requirements

MOSAIC Aerosol Module

- **Mo**del for **S**imulating **A**erosol **I**nteractions and **C**hemistry (Zaveri et al., 2008)
- Comprehensive aerosol module for air quality and climate modeling
- Flexible framework for coupling various gas and aerosol processes
- Robust, accurate, and highly efficient custom numerical solvers for several 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 – **planned**

Thermodynamics & Ma… 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)	$2NaHSO_4(s) + NH_3(g) \rightarrow Na_2SO_4(s) + NH_4HSO_4(s)$

- **Custom numerical techniques have been developed to solve these equations efficiently and accurately**

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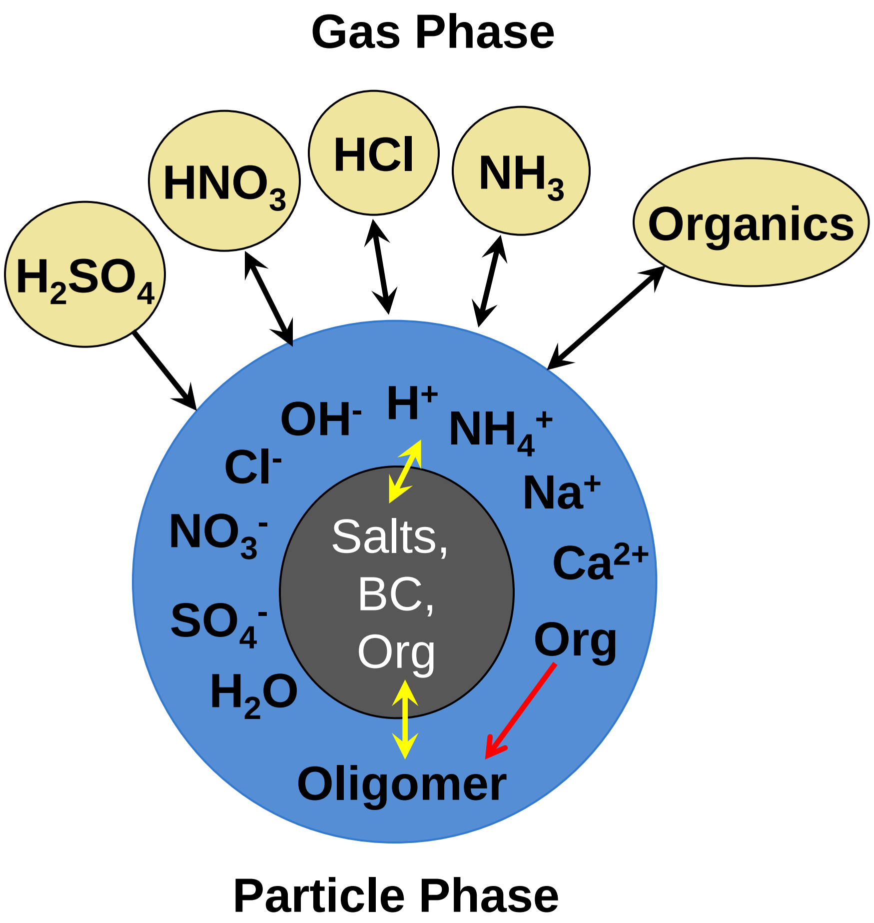
Gas-Particle Partitioning of Organics

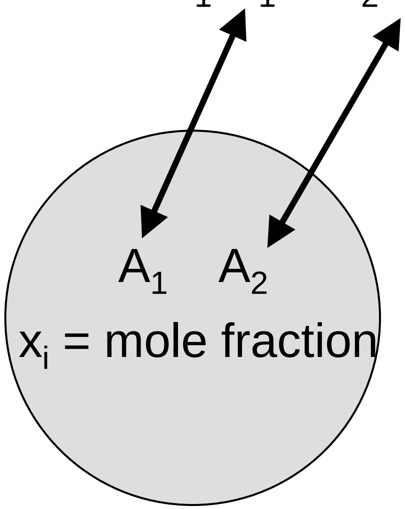
- Organic-inorganic interactions within the particle to determine water uptake and phase separation (partially implemented)
- Size-distributed, dynamic mass transfer between gas and particles
  - Raoult's Law in the absence of aqueous phase (implemented)
  - Reactive uptake that instantly converts VOC to non-volatile products (implemented)
  - Henry's Law in the presence of aqueous phase (future)
  - Particle-phase reactions (future)



Raoult's Law vs. Reactive Uptake

Raoult's Law Based Mass Transfer

$HC + \text{oxidant} \rightarrow \alpha_1 G_1 + \alpha_2 G_2$

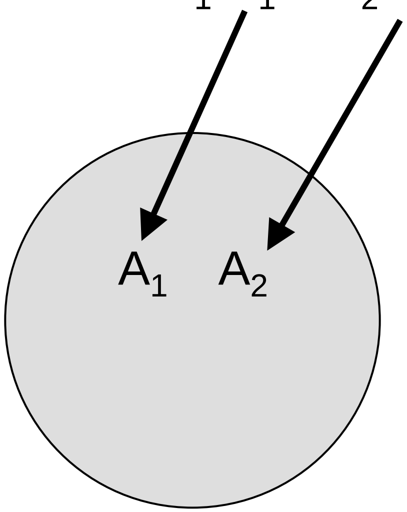


$$\frac{dG_i}{dt} = -k_i\,(G_i - x_i P_i^0)$$

vapor pressure

Reactive Uptake Mass Transfer

$HC + \text{oxidant} \rightarrow \alpha_1 G_1 + \alpha_2 G_2$



$$\frac{dG_i}{dt} = -k_i G_i$$

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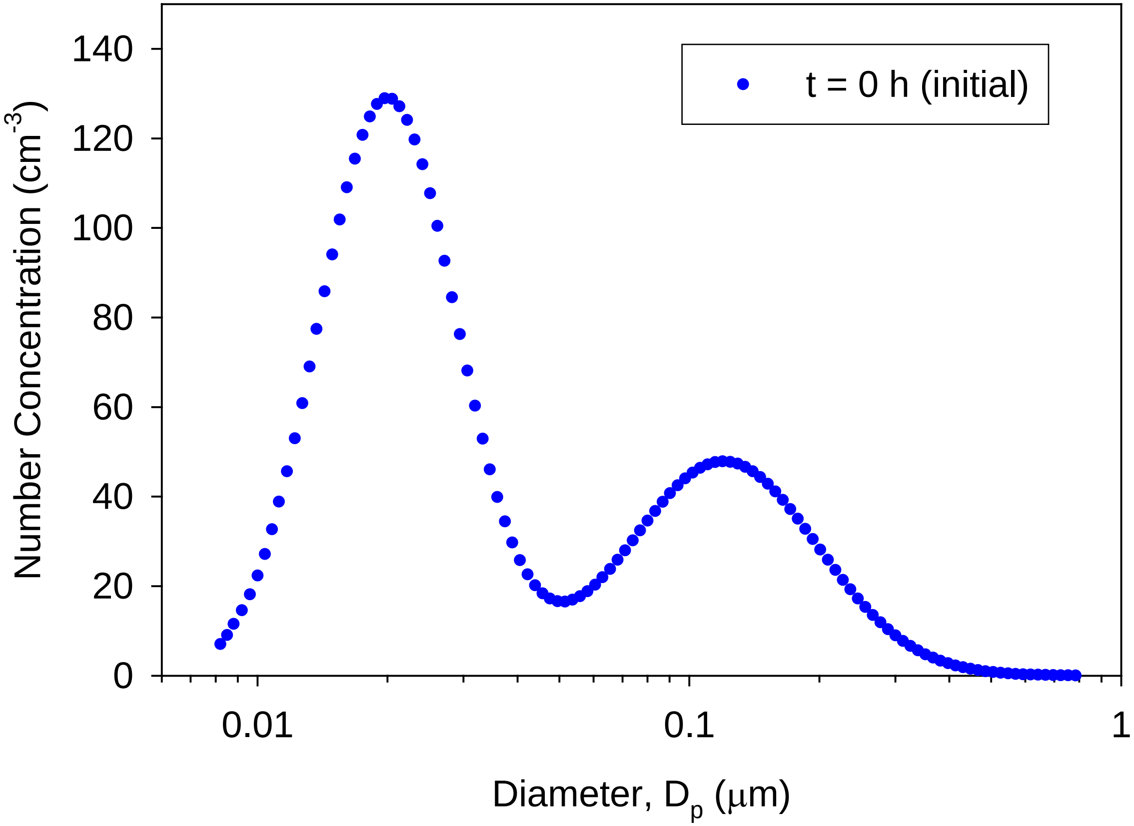
Sample Results

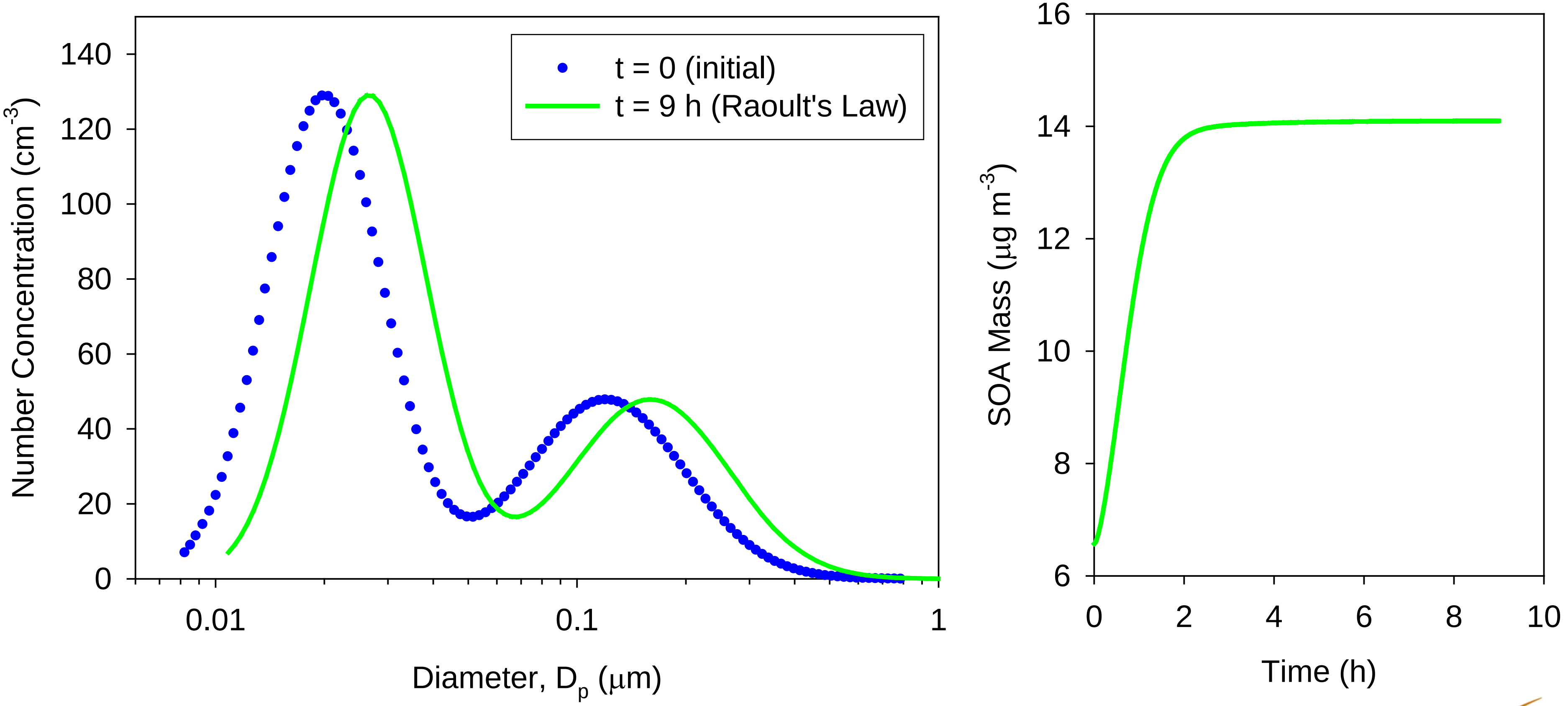
- Idealized Case
- Sacramento Urban Air Case

Idealized Case



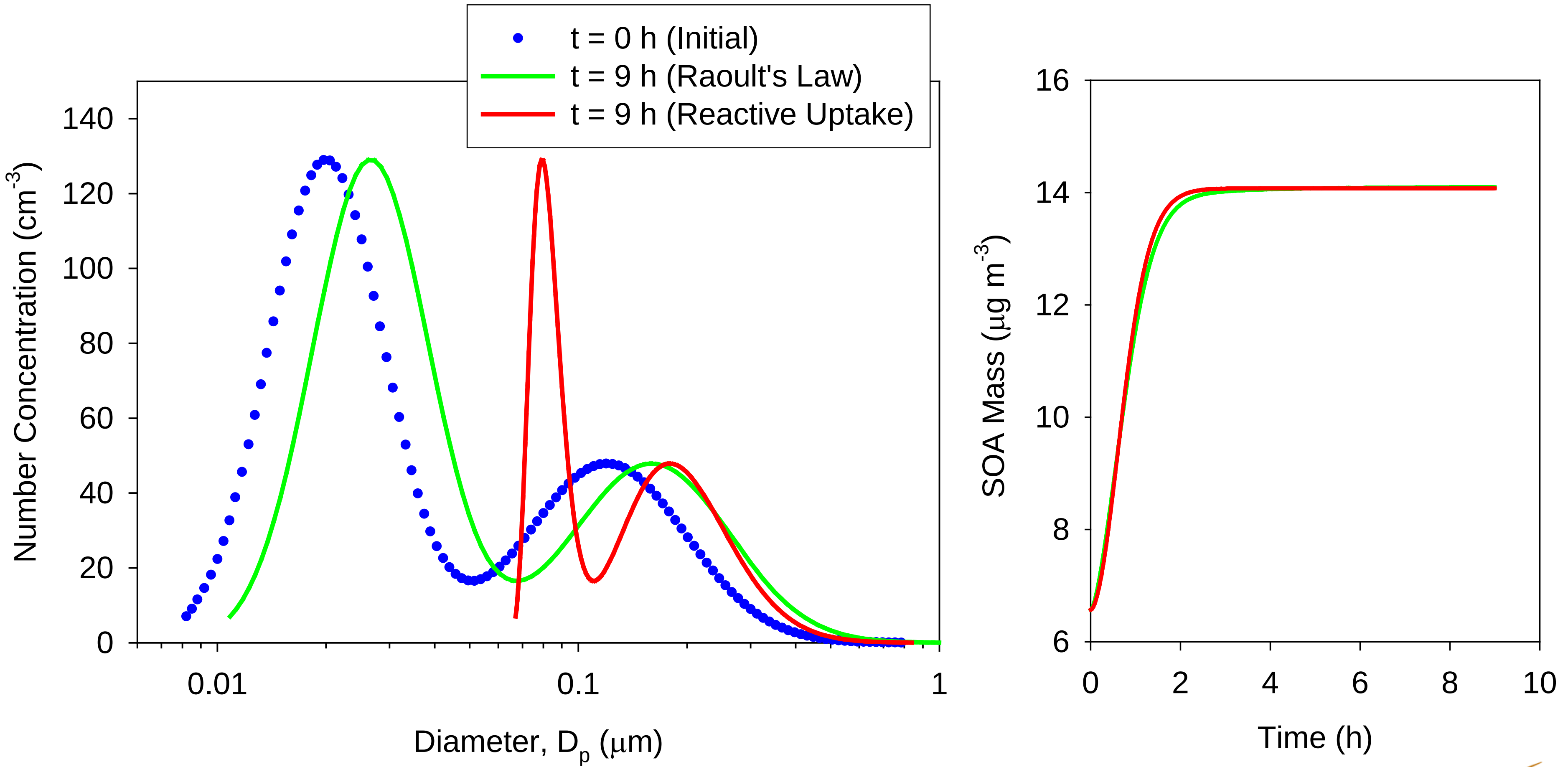
Initial aerosol composition: mass ratio $OA/(NH_4)_2SO_4 = 1$

Idealized Case



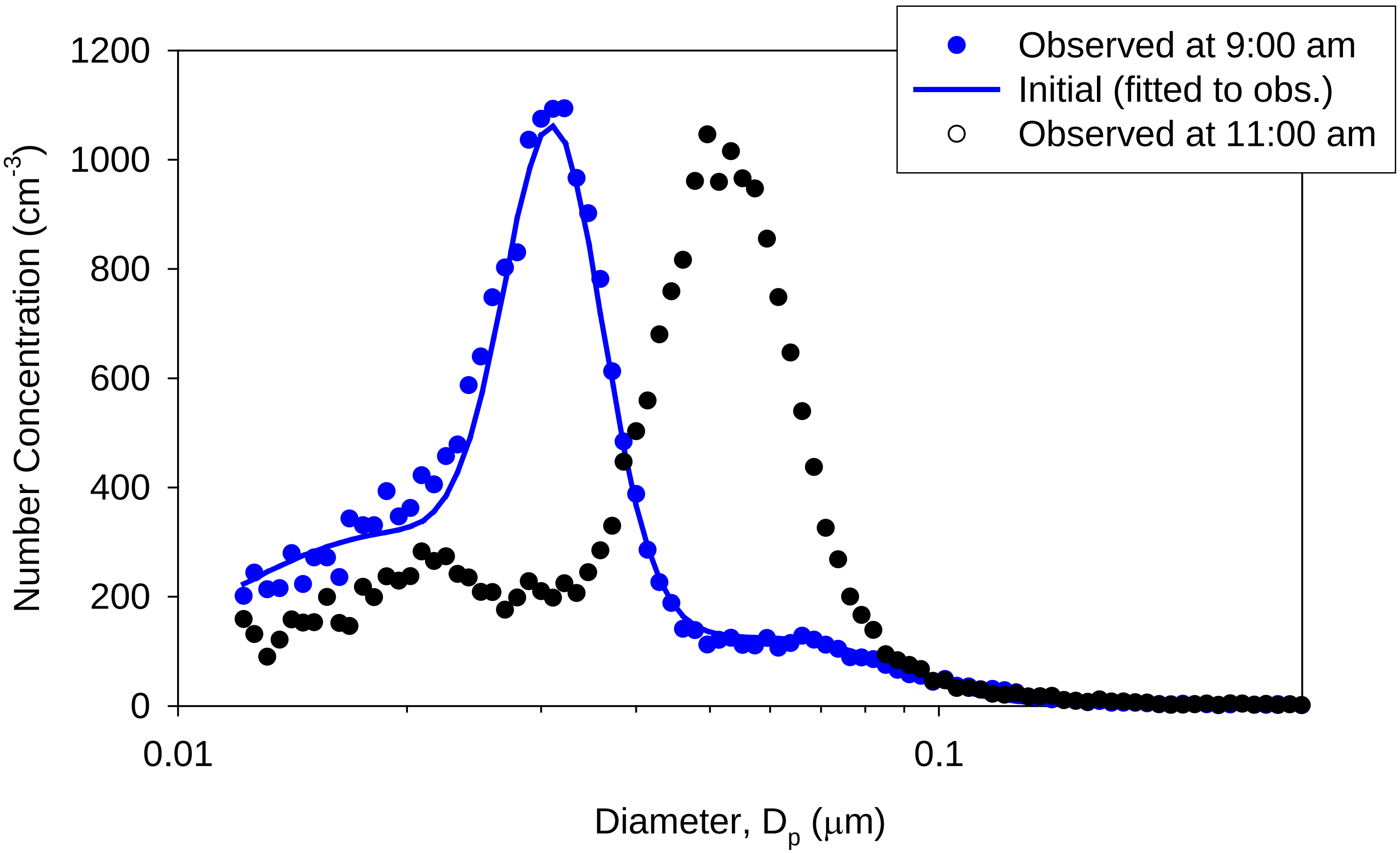
Initial aerosol composition: mass ratio $OA/(NH_4)_2SO_4 = 1$

Idealized Case



Initial aerosol composition: mass ratio OA/$(NH_4)_2SO_4$ = 1

Sacramento June 6, 2010



Initial aerosol composition: mass ratio $OA/(NH_4)_2SO_4 = 10$

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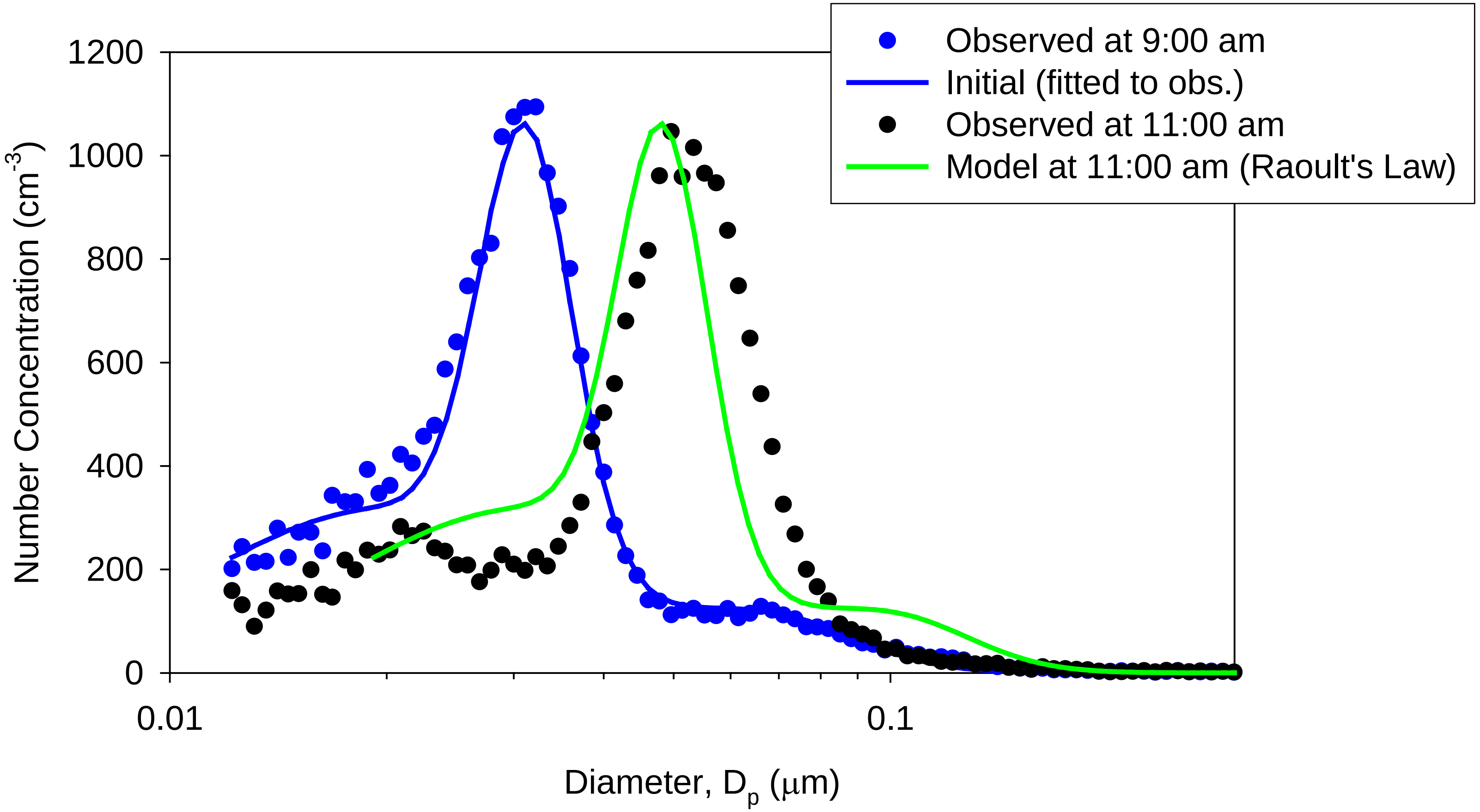
Sacramento June 6, 2010



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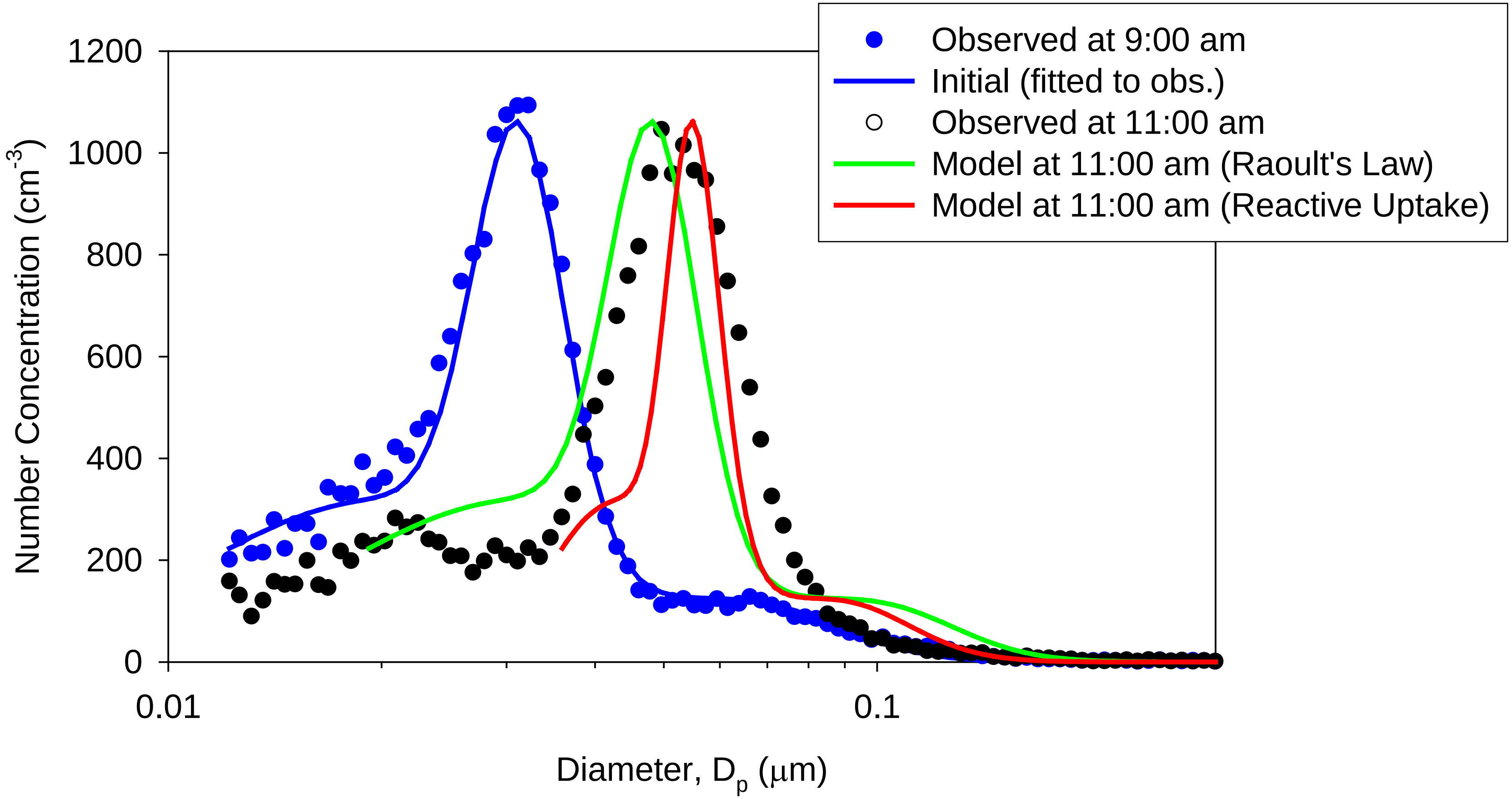

Initial aerosol composition: mass ratio $OA/(NH_4)_2SO_4 = 10$

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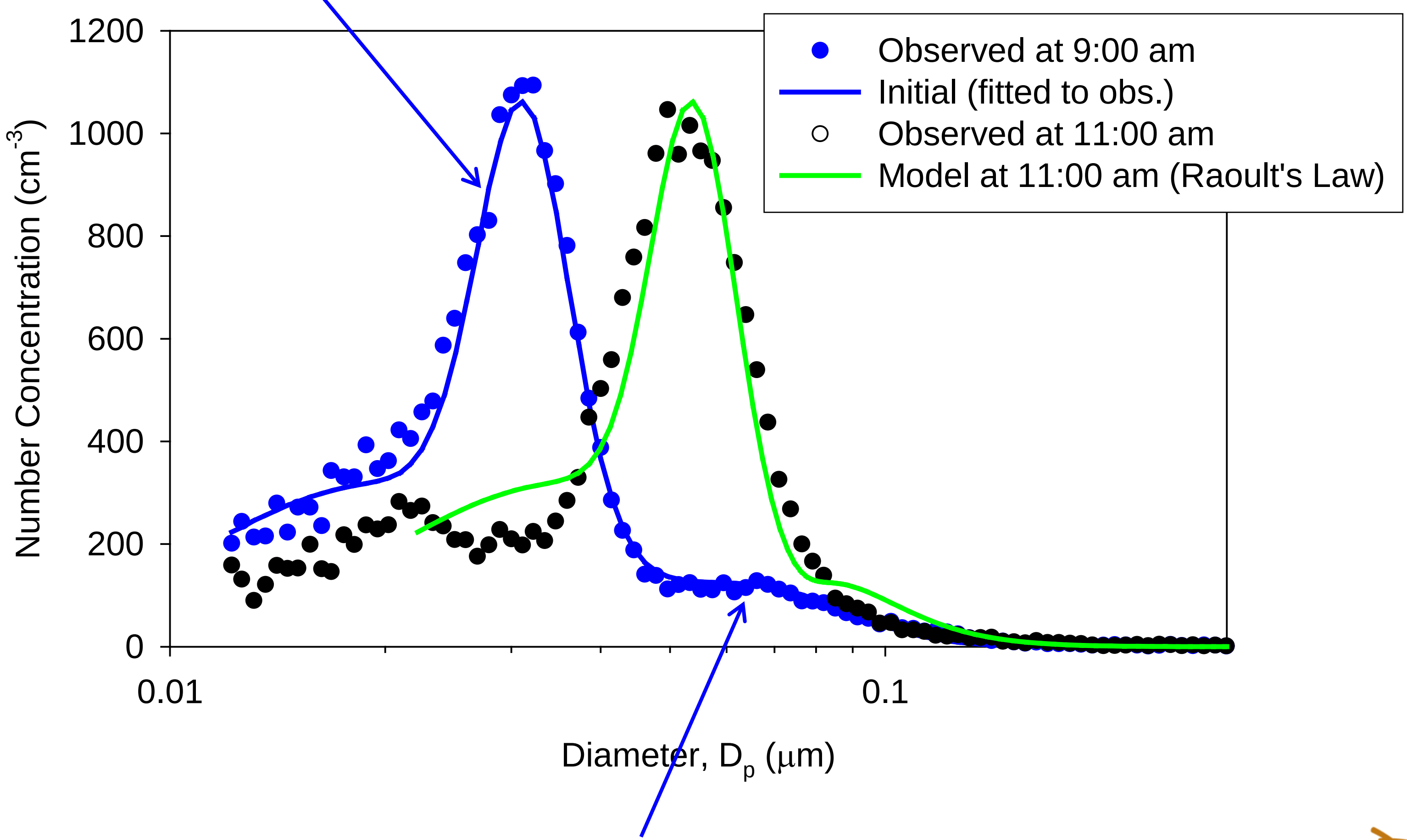
Aitken mode mass ratio $OA/(NH_4)_2SO_4 = 10$



Accumulation mode mass ratio $OA/(NH_4)_2SO_4 = 0.01$

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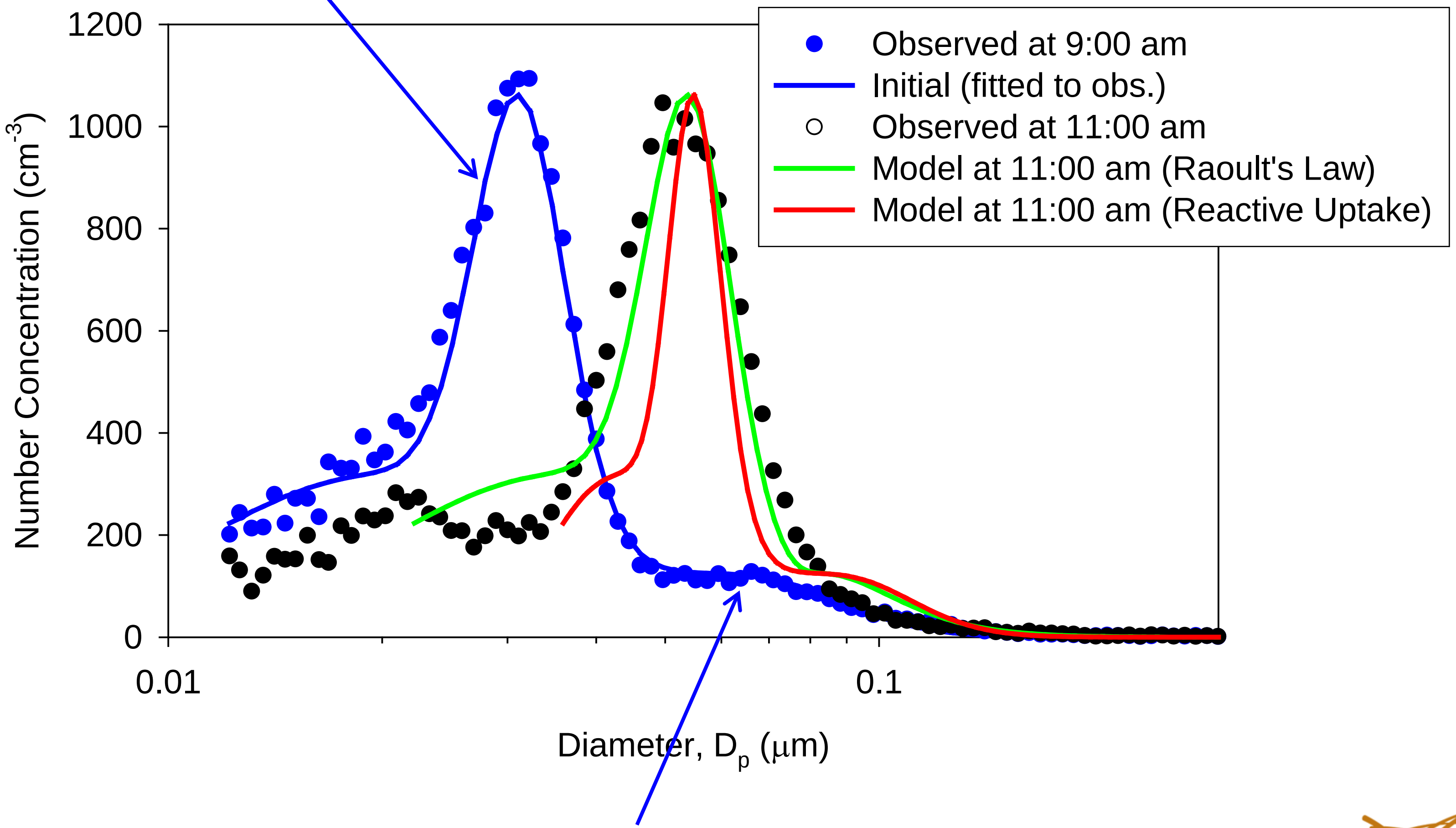
Aitken mode mass ratio $OA/(NH_4)_2SO_4$ = 10



Accumulation mode mass ratio $OA/(NH_4)_2SO_4$ = 0.01

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Future Directions

- Perform additional constrained Lagrangian model analyses to test different SOA formation mechanisms
- Use carefully designed chamber experiments to constrain and evaluate different formulations
- Extend model analyses to mixtures of organic and inorganic species at different relative humidities
- Implement and evaluate new SOA formulations in WRF-Chem using urban to regional field observations

Thank you for your attention

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ASR Atmospheric System Research

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