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A detailed aerosol mixing state model for investigating interactions between mixing state, semivolatile partitioning, and coagulation

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**Interactions: mixing
state, semivolatile
partitioning, and
coagulation**

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

A new method for describing externally mixed particles, the Detailed Aerosol Mixing State (DAMS) representation, is presented in this study. This novel method classifies aerosols by both composition and size, using a user-specified mixing criterion to define boundaries between compositional populations. Interactions between aerosol mixing state, semivolatile partitioning, and coagulation are investigated with a Lagrangian box model that incorporates the DAMS approach. Model results predict that mixing state affects the amount and types of semivolatile organics that partition to available aerosol phases, causing external mixtures to produce a more size-varying composition than internal mixtures. Both coagulation and condensation contribute to the mixing of emitted particles, producing a collection of multiple compositionally distinct aerosol populations that exists somewhere between the extremes of a strictly external or internal mixture. The selection of mixing criteria has a significant impact on the size and type of individual populations that compose the modeled aerosol mixture.

1 Introduction

Aerosol impacts on health, visibility, climate, and cloud formation, are governed by particle composition, size, and mixing state. For example, particles of different composition have been shown to exhibit different cloud condensation nuclei (CCN) behavior (Broekhuizen et al., 2004; Corrigan and Novakov, 1999) and Lesins et al. (2002) found that optical properties influencing radiative forcing for internal and external mixtures of black carbon and ammonium sulfate could differ by over 50%. In order to correctly assess the effects of atmospheric aerosols it is essential to know their composition and mixing state and understand how these properties change with time.

Many measurement studies have shown that particles emitted from different sources have distinct compositions (Rogge et al., 1993; Chow et al., 2004). Thus, aerosol

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

emissions enter the atmosphere as an external mixture of compositionally distinct populations. However, aerosol mixing state is not constant, but evolves over time. As particles interact with each other and with the gas phase, they become more compositionally similar and resemble an internal mixture. Single particle measurements have helped illuminate this transition from external to internal mixing. Hasegawa and Ohta (2002), for example, found that in urban areas, where emissions sources are nearby, soot particles were externally mixed, but in non-urban areas, where particles had undergone long range transport, internal mixtures of soot and water soluble materials were more common. Naoe and Okada (2001) examined aerosol mixing state at an urban site and found that the number fraction of internally mixed particles increased with particle size (2–12% internally mixed for 0.02–0.03 μm particles vs. 17–74% for the 0.1–0.2 μm size range), indicative of mixing due to particle growth.

These changes in aerosol mixing state are most likely due to secondary aerosol formation. Semivolatile products formed in the gas phase are able to partition to any particles present in the atmosphere. Over time this has the effect of adding secondary aerosol mass to initially distinct populations, making them more similar in composition. Additionally, semivolatile compounds will continue to repartition, maintaining a balance between different aerosol populations via equilibrium with a common gas phase, even as new particles are emitted.

Aerosol mixing state is also influenced by coagulation. When particles of different compositions coalesce the resulting particle will be a mixture of the two original compositions. The actual degree of mixing that occurs depends on the relative sizes of the coagulating particles. If one particle is much smaller than the other, the coagulated particle will have a composition very similar to that of the original large particle. Significant mixing only occurs when the colliding particles are of similar size. Jacobson calculated that for moderately polluted conditions, most emitted particles will become internally mixed to some degree within a few hours due to coagulation (Jacobson, 2002).

Just as partitioning can influence mixing state, mixing state can have a large effect on how semivolatile partitioning occurs. Kleeman et al. (1997) have shown that

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

with semivolatile inorganics a bimodal size distribution can be created due to hygroscopic particles growing more quickly than hydrophobic particles of similar initial size as relative humidity increases. Such bimodal distributions are observed in atmospheric measurements, but could not be reproduced by assuming an internal mixture. They also found differences in the amount of aerosol nitrate formed for internal and external mixtures. Similar behavior occurs with semivolatile organics, where polar organics will partition preferentially to an aqueous aerosol phase, while nonpolar organics will be absorbed mainly by a more nonpolar organic aerosol phase (Griffin et al., 2003; Pun et al., 2002).

Traditionally, air quality models have treated aerosols as an internal mixture. Unfortunately, assuming an incorrect mixing state can artificially distort the aerosol size and component distribution (FassiFihri et al., 1997; Kleeman et al., 1997; Jacobson, 2001, 2002). Recently, other approaches for describing external mixtures have been used in models developed by Kleeman (Kleeman et al., 1997; Bhawe et al., 2002; Ying et al., 2004, 2007), Jacobson (2001, 2002), and Riemer et al. (2008). The Kleeman source-oriented external mixture trajectory model represents the aerosol with thousands of particle classes according to particle size, emission source category, and time of emission. These distinct populations interact with the same gas phase, but evolve independently based on their unique compositions. The model does not account for coagulation, which was considered to have a negligible effect on aerosol mass distributions for urban time scales. When considering aerosol number or ultrafine particles, however, coagulation is a significant process that must be included (Binkowski and Roselle, 2003; Jacobson, 1997a; Jung and Kim, 2006; Yao et al., 2005).

Jacobson's approach describes the aerosol with several single source populations that interact with the gas phase and with each other to form additional mixed composition populations. Over time, emissions are added to the source populations, and when coagulation or condensation occurs, mass is transferred to the appropriate mixed population. In accounting for coagulation it places all binary mixtures into the same distribution, regardless of the relative amounts of each component. As a result, the mixed

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

population containing components A and B will include both particles that have 99% A, 1% B and particles that have 1% A, 99% B.

The PartMC model developed by Riemer et al. (2008) is a particle-resolved Monte Carlo model that tracks the composition of individual particles within a single cell Lagrangian framework. It accounts for condensation and coagulation involving a population of $\sim 10^5$ particles, with coagulation treated using a new efficient stochastic method. With such a high level of detail it is computationally demanding, but provides a numerical benchmark against which lower resolution mixing state models can be compared.

This paper presents a new modeling method for representing externally mixed particles. The detailed aerosol mixing state (DAMS) representation classifies particles by both size and composition, providing a level of compositional detail that can distinguish between external and internal mixtures. The DAMS approach, along with corresponding coagulation and condensation routines, is incorporated into a box model and used in simulations of a simplified atmospheric scenario. Model predictions of aerosol size and component distributions are compared between internal and external mixtures to demonstrate the impact of mixing state on aerosol growth and evolution. Simulations with and without coagulation, and using different mixing state criteria are also compared to further illustrate the interactions between aerosol mixing state, semivolatile partitioning, and coagulation.

2 Model formulation

2.1 Model framework

The model and simulations in this study were designed to provide a simple scenario for testing the new aerosol mixing state method and for initial investigations of the interactions between aerosol mixing state, semivolatile organic partitioning, and coagulation. A Lagrangian box model was used to simulate the evolution of aerosol size and composition distributions over time as semivolatile organics partition onto emitted organic

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



and inorganic particles, particles coagulate with each other, and particles and gases are removed by dilution with clean air. Future studies based on results of this work are planned with more complex models capable of representing atmospheric scenarios in greater detail.

- 5 The model is an extension of previous aerosol models (Bowman et al., 1997; Bowman and Melton, 2004; Sheehan and Bowman, 2001; Bowman and Karamalegos, 2002), with updated treatments of the aerosol representation method and the coagulation process. Semivolatile organic partitioning is modeled as an absorption process (Pankow, 1994a, b), and is described by a partitioning coefficient, K_i ,

$$10 \quad K_i = \frac{A_i}{M_t G_i} \quad (1)$$

- which is the ratio of the aerosol-phase concentration, A_i , and the gas-phase concentration, G_i , of semivolatile compound i , normalized by the total concentration of absorbing material, M_t . As shown by Pankow (1994b), the absorptive partitioning coefficient can be expressed as a function of physical and thermodynamic properties of the semivolatile compound

$$15 \quad K_i = \frac{RT}{MW \gamma_i p_i^\circ} \quad (2)$$

where R is the ideal gas constant, T is temperature, MW is the mean molecular weight of the absorbing aerosol phase, γ_i is the activity coefficient of component i in this phase, and p_i° is the vapor pressure of product i as a pure liquid.

- 20 The temperature and composition dependence of the partitioning coefficient can be described using an expression for K_i at a given set of T , MW , and γ_i conditions relative to a reference value of the partitioning coefficient, K_i^* , at a set of reference T^* , MW^* , and γ_i^* conditions (Bowman and Karamalegos, 2002)

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

$$K_i = K_i^* \left(\frac{MW^*}{MW} \right) \left(\frac{V_i^*}{V_i} \right) \left(\frac{T}{T^*} \right) \exp \left[\frac{H_i}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \right] \quad (3)$$

where H_i is the enthalpy of vaporization of component i .

Mass transfer between gas and particle phases is calculated using a dynamic partitioning approach. The mass flux J_{ij} of semivolatile compound i to particles in size section j is written as (Wexler and Seinfeld, 1990)

$$J_{ij} = n_j \frac{2\pi D_{pj} D_i}{1 + \frac{2\lambda}{\alpha_i D_{pj}}} (G_i^{\text{bulk}} - G_{ij}^{\text{eq}}) \quad (4)$$

where n_j is the number concentration of particles in section j , D_{pj} is the particle diameter in section j , D_i is the gas-phase diffusivity of compound i , λ is the air mean free path, and α_i is the accommodation coefficient of species i on the particle. G_i^{bulk} is the concentration of i in the bulk gas phase, and G_{ij}^{eq} is the gas-phase concentration of component i in equilibrium with aerosol particles in section j , which is calculated from Eq. (1)

$$G_{ij}^{\text{eq}} = \frac{A_{ij}}{M_{t,j} K_{ij}} \quad (5)$$

where A_{ij} is the aerosol phase concentration of component i in section j , $M_{t,j}$ is the total absorbing aerosol mass concentration in section j , and K_{ij} is the partitioning coefficient defined by Eq. (3) for component i in section j .

A key feature of the model is a new representation of the aerosol distribution which classifies particles into discrete bins based on both size and composition, with sufficient resolution to distinguish between different compositional mixtures. Condensational growth and coagulation routines have also been developed for use with the new aerosol representation. Adapted from Jacobson (1997b, 2002), these approaches move particles into the appropriate size and compositional bins as their size and/or

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

composition change due to condensation of semivolatile vapors and coagulation with other particles. The mathematical details of these novel methods are described in the following sections.

2.2 Detailed aerosol mixing state representation

5 To better represent externally mixed particles, a new sectional approach, the detailed aerosol mixing state (DAMS) representation, is developed that categorizes compositional mixtures into different populations such that particles are divided into discrete bins based on both size and composition. This new scheme is similar to that used by Jacobson (2001, 2002), but expanded to provide greater compositional detail. A unique
10 population exists for every possible combination of aerosol mixture components. For example, in a ternary system of components A, B, and C, there would be 7 populations as shown in Fig. 1.

An important feature of the DAMS representation is that it can distinguish between particles that are truly mixed, i.e., containing significant fractions of different components, and ones that, while technically a mixture, contain only small amounts of other components. For each aerosol component a threshold mass fraction, c_i , is specified that defines what is considered a significant amount of an individual component. For the 3-component system in Fig. 1, if the threshold is set at 5% for all components, particles in the AB population will contain at least 5% A and 5% B, but less than 5% C.
20 Particles in the A, B, or C populations will be mostly a single component, but may also contain small amounts (below the specified threshold) of other compounds.

The DAMS approach can be applied to aerosol mixtures with any number of components. In general, for a mixture with N_C components the total number of aerosol populations, N_P , will be

$$25 \quad N_P = 2^{N_C} - 1 \quad (6)$$

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The populations can be conveniently ordered and defined by specifying the index number of a given population, N , as

$$N = \sum_{q=1}^{N_c} 2^{q-1} g(q) \quad (7)$$

where $g(q)$, a function indicating if the mass fraction of component q , x_q , exceeds the specified mixing threshold, c_q , is defined as

$$g(q) = \begin{cases} 1 & \text{when } x_q \geq c_q \\ 0 & \text{when } x_q < c_q \end{cases} \quad (8)$$

To ensure that a population exists for all possible compositions, the individual mixing threshold values are subject to the constraint that $\sum c_q \leq 1$. Following the notation of Jacobson (1994), the total volume concentration of particles in bin Nk , corresponding to population type N and particle size range k is denoted by v_{Nk} , and the volume concentration of component q in that bin is denoted by $v_{q,Nk}$. Similarly, the number concentration in that bin is described as n_{Nk} . Thus, with the DAMS representation, an externally mixed aerosol is divided into bins that are classified by both composition and size.

2.3 Condensation

When condensational growth causes the aerosol to move in composition and size space, aerosol mass and number need to be transferred to the appropriate bin. For this study we have used the moving center approach (Jacobson, 1997a) where the characteristic volume of a bin u_{Nk} , is calculated from the total aerosol volume and number within the bin

$$u_{Nk} = \frac{v_{Nk}}{n_{Nk}} \quad (9)$$

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

and is allowed to vary between the fixed size boundaries of the bin. Similarly the aerosol composition within a bin is allowed to vary between the fixed compositional boundaries of the bin defined by the mixing thresholds c_q . When particle composition and/or size change beyond the defined limits of a given bin, all particles in the bin are transferred to the correct bin for their new size and/or composition. The total particle number, n_{Nk} , and component volumes, $v_{q,Nk}$, from the original bin are added to those already present in the new bin and a new characteristic size and composition for the bin are calculated. Since both sets of particles have a size and composition that lie within the boundaries of the bin, when they are combined together the resulting average size and composition will also be within the bin boundaries.

2.4 Coagulation

Coagulation will also cause particles to move in composition and size space. Unlike the coagulation of an internal mixture, where only particle size is a concern, the coagulation process for an external mixture is much more complex. Coagulation combines particles with different sizes and compositions, and the resulting aerosol must be assigned to both the correct size section and the correct compositional population.

The coagulation scheme used here is based on the approach developed by Jacobson (1997b, 2002). Coagulation is permitted to occur between all of the size and composition bins. The coagulated particle size will not, in general, be exactly equal to the particle size of any bin, but will fall somewhere between the particle sizes of two adjacent size bins. When this occurs, a fraction of the coagulated aerosol is assigned to each of these two destination size bins. This is done in such a way that the particle sizes in both the source and destination bins do not change. In the source bins, aerosol volume and number are reduced, and in the destination bins they are increased, with total aerosol volume being conserved, and total aerosol number reduced consistent with the loss of particle number due to coagulation.

A key difference between our coagulation procedure and that used by Jacobson is the manner in which coagulated aerosol is assigned to a compositional population.

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

In the work of Jacobson, particles are only allowed to move to more internally mixed populations. For example, when particles from population A and from population B coagulate, the resulting particle will be assigned to the mixed population AB. Aerosol from a mixed population will never be moved to a less mixed population. With the DAMS approach, however, it is possible for aerosol to move in both directions between more and less well mixed populations. For example, when a very small particle from population AB coagulates with a much larger particle from population A, the newly coagulated particle may only contain a small amount of B. If the concentration of B is below the mixing threshold, then the newly formed particle will be assigned to population A. As will be discussed below, this has important implications in the how the coagulation equations are solved.

The mathematical formulation for calculating coagulation in DAMS follows from previously developed coagulation models (Jacobson et al., 1994; Seinfeld and Pandis, 1998; Jacobson, 1997a, 2002), with adaptations to account for the expanded representation of aerosol mixing state. The volume concentration of component q in a bin for population type N and particle size range k at time t , $v_{q, Nk, t}$, can be written using the notation of Jacobson as:

$$v_{q, Nk, t} = \frac{v_{q, Nk, t-\Delta t} + \frac{1}{2} \Delta t \sum_{L=1}^{N_p} \sum_{M=1}^{N_p} \sum_{j=1}^k \sum_{i=1}^{k-1} f_{Li, Mj, Nk, t} \beta_{Li, Mj, t} v_{q, Li, t} n_{Mj, t}}{1 + \Delta t \sum_{L=1}^{N_p} \sum_{S=1}^{N_S} (1 - f_{Li, Nk, Nk, t}) \beta_{Li, Nk, t} n_{Li, t}} \quad (10)$$

where $v_{q, Nk, t-\Delta t}$ is the volume concentration of component q in bin Nk for population N and size k at time $t-\Delta t$, Δt is the time step size, $f_{Li, Mj, Nk, t}$ is the fraction of the particle volume formed by coagulation between bins Li and Mj that is assigned to bin Nk at time t , $\beta_{Li, Mj, t}$ is the coagulation kernel between bins Li and Mj at time t , and N_S is the total number of particle sizes.

The volume fraction $f_{Li,Mj,Nk,t}$ is defined as (Jacobson, 1997b)

$$f_{Li,Mj,Nk,t} = \begin{cases} \left(\frac{u_{Nk+1,t} - V_{Li,Mj,t}}{u_{Nk+1,t} - u_{Nk,t}} \right) \frac{u_{Nk,t}}{V_{Li,Mj,t}} & u_{Nk,t} \leq V_{Li,Mj,t} < u_{Nk+1,t} \quad k < N_S \\ 1 - f_{Li,Mj,Nk-1,t} & u_{Nk-1,t} < V_{Li,Mj,t} < u_{Nk,t} \quad k > 1 \\ 1 & V_{Li,Mj,t} \geq u_{Nk,t} \quad k = N_S \\ 0 & \text{all other cases} \end{cases} \quad (11)$$

where $V_{Li,Mj,t} = u_{Li,t} + u_{Mj,t}$ is the volume of a single particle created from coagulation of a particle from bin Li and a particle from bin Mj . The volume fraction in Eq. (11) divides the volume of a coagulated particle between two adjacent size bins, with each portion taking on the characteristic volume of the destination bin. As a result, the characteristic volumes for each bin do not change during the coagulation calculation.

Brownian diffusion is assumed the dominant coagulation mechanism in this study, with the coagulation kernel (β , $\text{cm}^3 \text{ particle}^{-1} \text{ s}^{-1}$) calculated based on Fuchs equation (Jacobson, 1997a; Seinfeld and Pandis, 1998). The total volume concentration in bin Nk at time t , $v_{Nk,t}$, is the sum of the individual component values

$$v_{Nk,t} = \sum_{q=1}^{N_C} v_{q,Nk,t} \quad (12)$$

and the number concentration of particles in bin Nk , $n_{Nk,t}$, is calculated from the total volume concentration and the characteristic single particle volume in the bin

$$n_{Nk,t} = \frac{v_{Nk,t}}{u_{Nk,t}} \quad (13)$$

Because particles do not always move to more mixed populations, a noniterative semi-implicit approach where coagulation to and from less mixed populations is calculated before more-mixed populations (Jacobson, 2002), can not be used. Instead, Eq. (10) is fully implicit and is solved iteratively. The volume, $v_{Nk,t}$, and number, $n_{Nk,t}$, concentrations for each bin are updated by Eqs. (12) and (13) using volume and number concentrations from the previous iteration. Values from the previous time step are

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

used as initial guesses for the first iteration. For this study iterations were continued until the relative difference in volume concentration between two consecutive iterations was less than 0.1% for all bins. This convergence criteria value was selected to provide a balance of accuracy and calculation speed for a relatively simple aerosol system, but its influence on model performance has not yet been systematically evaluated. Work is ongoing to improve computational efficiency of the entire coagulation code and to determine optimum convergence criteria for more complex and computationally demanding aerosol systems.

3 Model simulations

Model simulations were performed using a simplified base case scenario, patterned after a polluted urban environment. While sufficient detail was included to test the new aerosol mixing state method and to enable a qualitative investigation of mixing state, partitioning, and coagulation interactions, it is important to note that this scenario is not meant to represent specific atmospheric conditions.

Simulation parameters for the base case scenario are summarized in Table 1. Primary particulate (PO1, PO2, INERT) and semivolatile vapors (SV1, SV2) are emitted at a constant rate into the model volume. Dilution of the air parcel with clean air removes particles and semivolatile vapors at a constant rate of $5.0\% \text{ h}^{-1}$. Gas-particle mass transfer calculations assume an accommodation coefficient of unity. Temperature varies with a fixed diurnal cycle ranging from 15 to 35°C . Emission rates were specified so as to produce a total fine particle concentration of approximately $60 \mu\text{g m}^{-3}$, with approximately $30 \mu\text{g m}^{-3}$ of organic aerosol. Together, the constant emissions, constant dilution, and diurnal temperature cycle result in a repeating steady state after the model has run for several days. To capture the full evolution of all particle distributions, the system was simulated for an 8 day period, and model results from the final day were analyzed. Additional simulation time did not noticeably change the bulk aerosol mass,

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

number, and composition or its distribution among the different size and composition bins.

A five component mixture was used to represent the aerosol phase in the base case scenario. The components and their partitioning properties are listed in Table 2. Primary organic aerosol is represented by heneicosane and levoglucosan, which are key components from diesel soot (Schauer et al., 1999; Chow et al., 2007) and wood smoke (Schauer et al., 2001) emissions, respectively. Heneicosane, model compound PO1, is nonpolar whereas levoglucosan, model compound PO2, is relatively polar. PO1 and PO2 are both assumed to be nonvolatile and remain almost entirely in the aerosol phase. Semivolatile organic aerosol is represented in the scenario by heptadecanoic acid, SV1, and norpinonic acid, SV2, compounds with relatively low and high polarity, respectively. One general inert compound, that is nonvolatile and does not interact with the organic components, is used to represent all other aerosol components. The highly simplified representation of aerosol composition chosen for this initial study provides a relatively small number of mixture populations and allows the general qualitative behavior of the system to be more clearly seen. Future studies targeted at simulating realistic atmospheric conditions will more accurately describe atmospheric aerosol composition by including individual inorganic compounds, water, and other organics, and will better account for the interactions between these components.

The aerosol distribution can be simulated as either an internal or an external mixture. In all cases, the size distribution uses 10 size sections, with mean diameters logarithmically spaced from 0.02 to 2.5 μm . For an internal mixture, there is a single well-mixed aerosol population throughout the entire simulation. The initial population, shown in Fig. 2, has a peak near 0.09 μm and contains PO1, PO2, and INERT, with total concentration of 18.0 $\mu\text{g m}^{-3}$. The initial mixture is one third organic, with equal amounts of PO1 and PO2. Particulate emissions during the simulation have the same composition and size distribution as the initial distribution.

For an external mixture, multiple aerosol populations are simulated, each with different size and compositional distributions. With 5 components in the base case, there

**Interactions: mixing
state, semivolatile
partitioning, and
coagulation**

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

are a total of 31 possible compositional populations. The initial distribution contains only three populations, pure PO1, pure PO2 and pure INERT. Summed together, these populations are identical to the initial population used in the internal mixture case, with the same total mass and component distribution. During simulations, partitioning of SV1 and SV2 and coagulation alter the composition of these initial populations. When the composition changes beyond the specified limits for a given population, the aerosol is moved to one of the other compositional populations. In the base case scenario, the mixing threshold criterion, c , is set at 0.1 for all components. The influence of the mixing threshold value on simulation results is discussed further in Sect. 4.3.

4 Simulation results

4.1 Mixing state

Simulations were performed with the base case scenario for both an external and an internal mixture. The predicted distributions for external and internal mixtures are shown in Fig. 3 and Table 3. In both cases, the aerosol distribution shows growth to larger particle sizes and the addition of semivolatile components, but the specific growth behavior for external and internal mixture simulations is different. Since both simulations used the same base case scenario to define emissions and other input parameters, differences in model results are entirely attributable to the assumed mixing state.

When semivolatile components, SV1 and SV2, partition to the aerosol phase, their partitioning behavior can be strongly influenced by aerosol phase interactions. Because of their similar polarity, nonpolar SV1 prefers to condense on particles composed of nonpolar PO1, while polar SV2 is more likely to partition to polar PO2. When the aerosol is treated as an internal mixture, this partitioning difference between SV1 and SV2 is not seen, because all particles have the same percentage of PO1 and PO2. As a result, for an internal mixture particles of different sizes have the exact same composition, as shown in Fig. 3b. Because of its higher partitioning coefficient, more SV2

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



condenses to the aerosol phase than SV1, and there is a higher percentage of SV2 in each section.

For an external mixture, composition is not uniform, but varies with particle size. The total aerosol distribution, summed from the individual aerosol populations, with accompanying pie plots of the composition in each size section, is shown in Fig. 3a. Because more SV2 condenses to the particle phase than SV1, and SV2 partitions preferentially to PO2, particles made of PO2 grow slightly faster than those of PO1. As a result, higher fractions of PO2 and SV2 occur in the largest size sections. In smaller size sections, INERT dominates because no semivolatile organic components condense on it, and the movement of INERT to larger sizes only occurs through coagulation between particles.

The external mixture also causes a net reduction in semivolatile organic aerosol for these simulations. As shown in Table 3, the mass of component SV2 in the aerosol phase is $10.4 \mu\text{g m}^{-3}$ for the internal mixture, but only $8.62 \mu\text{g m}^{-3}$ for the external mixture. For SV1, the aerosol phase concentration remains essentially unchanged at $4.6 \mu\text{g m}^{-3}$. The partitioning behavior of these components depends on the amount of absorbing mass available and the chemical composition of the absorbing phase(s). For an internal mixture, there is a single uniform absorbing phase containing both nonpolar PO1 and polar PO2. This mixture of nonpolar and polar organics is not an optimum absorption medium for either nonpolar SV1 or polar SV2, but there is a relatively large absorbing mass available. For the external mixture simulation, PO1 and PO2 are largely segregated into different particle populations. Relative to the internal PO1/PO2 mixture, the PO1-dominated populations in the external mixture increase partitioning of SV1 and reduce partitioning of SV2, while the PO2-dominated populations have the reverse effect, decreasing SV1 partitioning and increasing SV2 partitioning. The net result of these competing effects is the observed decrease in partitioning to the aerosol phase for SV2 and the unchanged partitioning for SV1. As seen in this case, the effect of mixing state on partitioning is complex and will depend on the specific semivolatile compounds and absorbing aerosol phases present.

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Despite these changes in partitioning, the overall aerosol size distribution is similar for both external and internal mixtures, as shown in Fig. 3a–b. A major fraction of both distributions is composed of the nonvolatile model species INERT, PO1, and PO2. The differences in growth due to SV1 and SV2 partitioning that are seen in total and component mass concentrations are not large enough to significantly alter the size distribution. Scenarios where semivolatile inorganic compounds and water vapor also partition to the aerosol phase might result in a larger impact of mixing state on the overall size distribution, but semivolatile organics alone are not expected to contribute enough mass to produce such an effect.

The other clear difference between internal and external mixture simulations, is that the predicted composition of individual particles changes drastically. Unlike internally mixed particles where there is only 1 population with uniform composition, the external mixture simulations predict the formation of 9 major compositional populations as shown in Tabl 4 and Fig. 4a. Other mixture populations are also created by the model, but their mass and number concentrations are small enough to be negligible and are not reported here. Semivolatile partitioning and coagulation affect the original 3 populations in different ways. The original PO1 population disappears, and most PO1 mass is found in population 2 (PO1/SV1 mixture), and population 4 (PO1/SV1/INERT mixture). The PO1/SV1 mixture is formed when SV1 partitions to emitted PO1, while the PO1/SV1/INERT mixture is produced from both coagulation between PO1/SV1 and INERT populations or partitioning of SV1 to a coagulation-formed PO1/INERT population. Similarly, there is no PO2 population left, as most PO2 shifts to distributions 3 (PO2/SV2 mixture) and 5 (PO2/SV2/INERT mixture). The original INERT population, however, still exists with significant mass and number concentrations. Unlike the organic populations, SV1 and SV2 do not partition to INERT in this model, and mixing between INERT and the organic components occurs almost entirely through coagulation. Because there is a constant emission source of INERT particles and coagulation occurs on a relatively long time scale, only a fraction of the INERT component is transferred to other populations.

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

The other populations that are produced, most notably populations 7 (PO1/PO2/SV1/SV2/INERT) and 7a (PO1/PO2/SV2/INERT) which contain significant amounts of all (or most all) the aerosol components, arise from coagulation between already mixed populations. Since these populations are not formed directly from the original pure populations, they have somewhat lower mass and number concentrations. It is also important to recognize that once the simulation begins all populations contain at least small amounts of every component. For example, population 5 is labeled as a mixture of PO2, SV2, and INERT, but as can be seen in Fig. 4a, it also includes PO1 and SV1 at levels below the 10% mixing threshold. In some cases, subpopulations, such as 4b (PO1/SV1/SV2/INERT) and 7a (PO1/PO2/SV2/INERT), are denoted that contain either slightly more (SV2 in population 4b) or less (SV1 in population 7a) of one component.

4.2 Coagulation

Internal and external mixture simulations of the base case scenario were also run with coagulation processes turned off in the model. Comparison of results for simulations without coagulation (Fig. 3c–d and Tables 3 and 5) with simulations including coagulation (Fig. 3a–b and Tables 3 and 4) highlight the impact of coagulation on particle growth and mixing. As expected, coagulation lowers the number of particles, with both external and internal mixture total number concentrations reduced to approximately one third of their values without coagulation. At the same time, particle growth due to coagulation leads to broader size distributions with more particles growing to the larger size sections, as seen in Fig. 3. Total particle mass, however, is not affected as dramatically. The internal mixture simulations with and without coagulation both result in a total mass of $60.0 \mu\text{g m}^{-3}$. In contrast, the external mixture results in $58.2 \mu\text{g m}^{-3}$ with coagulation and $56.2 \mu\text{g m}^{-3}$ without. Differences in total mass are due solely to changes in the partitioning of SV1 and SV2 as emission and deposition of the primary species are the same in all simulations. As discussed in the previous section, for this simulation partitioning is reduced as the aerosol becomes more externally mixed. The

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



external mixture simulation without coagulation is the most externally mixed scenario and, consequently, predicts the lowest amount of semivolatile aerosol formation.

The most significant difference between the simulation results with or without coagulation is the number of compositional populations. For the internal mixture, there is always only one population, but for the external mixture, coagulation causes the number of major populations to increase from 3 to 9. When coagulation is neglected, there are no interactions between different populations, the initial 3 populations grow independently, and no new populations are formed. Since SV1 partitions almost exclusively to PO1 and SV2 to PO2, the populations undergo only partial mixing. As shown in Fig. 4b, one population contains only INERT, another mainly PO1 and SV1, and the third is composed of PO2 and SV2. When the simulation includes coagulation, however, the initial components are able to mix with each other and many new populations are created. As seen in Fig. 4a, a wide range of compositional mixtures is produced, with most populations containing at least minor amounts of each component.

4.3 Mixing criterion

In the base case simulations, a mass fraction of 0.1 was arbitrarily defined as the threshold for determining whether a component should be considered part of a mixture. In order to investigate the influence of this mixing threshold on simulation results, the base case scenario was run with the mixing threshold criterion, c , set as 0.02, 0.05, 0.1 and 0.2, and the simulated aerosol size and composition distributions were compared.

Simulation results showed that the size and component distributions are generally insensitive to the choice of mixing criteria. In all cases, the component distributions are similar, with a high percentage of INERT in smaller size particles while the larger particles have a higher fraction of organic components.

Where the specified mixing criterion does have a great effect is on the mass concentrations of the individual compositional populations, as shown in Table 6. When c is set to a low value of 0.02, population 7 (a mixture of all five compounds) has the highest mass concentration, and most of the mass is found in populations that are

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

mixtures of organics and INERT. As the mixing criterion increases, mass shifts to the less well-mixed populations because of the higher threshold for defining what constitutes a mixture. When the threshold is set as high as 0.2, population 7 contains no particles, mass is concentrated in a smaller number of major populations, and the majority of particle mass is found in population 1 (the “pure” INERT mixture).

These results from the high ($c=0.2$) and low ($c=0.02$) mixing criterion simulations show the limiting behavior that can be expected from the model. When the mixing criterion is small, only a small amount of a compound needs to be added to form a mixture, leading to a large number of “mixed” populations even though they may in reality be dominated by a single component. In the extreme case, where c approaches zero, all of the mass will move to the completely mixed population as soon as condensation or coagulation occurs. At the other limit, a large value for the mixing criterion will inhibit the formation of mixed populations, and only a few major populations will be produced. By forcing components into the less mixed populations, the intended definition of an external mixture will again be circumvented. Thus, to produce meaningful results, a reasonable value for the mixing criterion must be defined.

The definition of mixing criterion, c , depends on the system being modeled, and will be affected by the number, type, and concentration of compounds considered. For the current simulation system, the predicted distribution for $c=0.1$ appears to capture reasonably well the range of mixtures present. For more complex systems, where there is a much larger number of components, the mixing criterion would need to be much smaller, to reveal the effect of all the compounds. Additionally, when individual components are present at different concentrations it may be advantageous to specify a different mixing threshold for each compound instead of using a common value for all components. Understanding how to best define mixing criteria values for different systems is a focus of our ongoing research.

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

5 Conclusions

A new modeling method for describing externally mixed particles, the Detailed Aerosol Mixing State (DAMS) representation, has been developed. In this method, aerosol particles are classified by both size and composition, with a compositional population defined for every combination of aerosol mixture components and these populations divided into size sections. A mixing criterion is used to define boundaries between compositional populations, allowing DAMS to distinguish between particles that are truly mixed and ones that contain only small amounts of other components. The DAMS approach has been incorporated in a Lagrangian box model together with condensational growth and coagulation routines developed for use with the new representation.

Model results demonstrate that interactions between aerosol mixing state, semivolatile partitioning, and coagulation are significant. The assumption of aerosol mixing state affects the amount and types of semivolatile organics that partition to the available aerosol phases. And since the partitioning of semivolatile species is influenced by aerosol-phase composition, the compositionally distinct aerosol populations in an external mixture exhibit different growth rates, producing a more size-varying composition compared to internal mixtures.

Both coagulation and condensation contribute to the mixing of aerosol particles. Condensation of semivolatile compounds changes particle composition as a mixture of primary and secondary aerosol is formed. While semivolatile compounds may partition preferentially to particles of similar composition, they will condense to some extent on all particles present. Over time this has the effect of adding secondary aerosol mass to initially distinct populations, making them more similar in composition. Coagulation mixes together aerosol particles from different compositional populations and tends to move all particles to a single well-mixed population. Simulation results show that coagulation has a significant influence on aerosol evolution and should be included when modeling aerosol mixing state. The aerosol distribution produced by the combined effects of condensation, coagulation, and emissions is predicted to be a collection of

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

multiple compositionally distinct populations that exists somewhere between the extremes of a strictly external or internal mixture.

The selection of mixing criteria shows limited effects on the final size and compositional distribution of particles, but has a significant impact on the size and type of individual populations that compose the external mixture. Properly defining mixing criteria values depends on the number, type, and concentration of primary and secondary aerosol components present and on the aerosol properties targeted for study. Guidelines for criterion selection for more complex aerosol systems need to be investigated further.

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Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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**Interactions: mixing
state, semivolatile
partitioning, and
coagulation**

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Interactions: mixing
state, semivolatile
partitioning, and
coagulation**

J. Lu and F. M. Bowman

Table 1. Model parameters for base case scenario.

Particulate emission rates ($\mu\text{g m}^{-3} \text{h}^{-1}$)	PO1: 0.375 PO2: 0.375 INERT: 1.5
Semivolatile emission rates ($\mu\text{g m}^{-3} \text{h}^{-1}$)	SV1: 1.5 SV2: 1.0
Air parcel dilution rate ($\% \text{h}^{-1}$)	5.0
Accommodation coefficient	1.0
Temperature ($^{\circ}\text{C}$)	25 ± 10
Simulation time (h)	188
Mixing criterion	0.1

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Interactions: mixing
state, semivolatile
partitioning, and
coagulation**

J. Lu and F. M. Bowman

Table 2. Aerosol component properties.

Model Name	Component	K_i^* ($\text{m}^3 \mu\text{g}^{-1}$)	H_i (kJ mol^{-1})	MW_i (g mol^{-1})	Relative Polarity
PO1	Heneicosane	1.0×10^{12}	0.0	296	Low
PO2	Levogluconan	1.0×10^{12}	0.0	162	High
SV1	Heptadecanoic acid	0.0172	75	270	Low
SV2	Norpinonic acid	0.0420	75	170	High
INERT					

K_i^* values correspond to reference conditions of $T^*=298 \text{ K}$, $\text{MW}^*=150 \text{ g mol}^{-1}$, $\gamma_i^*=1$.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Table 3. Total number, mass, and component concentrations for base case scenario with external and internal mixtures, with and without coagulation.

Mixing State	With Coagulation		Without Coagulation	
	External	Internal	External	Internal
Total number ($\# \text{ cm}^{-3}$)	5.08×10^4	5.86×10^4	1.46×10^5	1.46×10^5
Total mass ($\mu\text{g m}^{-3}$)	58.2	60.0	56.2	60.0
INERT ($\mu\text{g m}^{-3}$)	30.0	30.0	30.0	30.0
PO1 ($\mu\text{g m}^{-3}$)	7.50	7.50	7.50	7.50
PO2 ($\mu\text{g m}^{-3}$)	7.50	7.50	7.50	7.50
SV1 ($\mu\text{g m}^{-3}$)	4.61	4.62	4.09	4.62
SV2 ($\mu\text{g m}^{-3}$)	8.62	10.4	7.14	10.4

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Table 4. Major populations* formed in base case scenario with an external mixture.

Index	Components					Mass ($\mu\text{g m}^{-3}$)	Number ($\# \text{cm}^{-3}$)
	INERT	PO1	PO2	SV1	SV2		
1	+					16.9	2.7×10^4
2		+		+		3.6	5.8×10^3
3			+		+	4.1	5.8×10^3
4	+	+		+		9.4	4.4×10^3
4b	+	+		+	+	1.1	2.8×10^2
5	+		+		+	12.9	5.0×10^3
6		+	+	+	+	0.9	4.3×10^2
7	+	+	+	+	+	3.0	4.9×10^2
7a	+	+	+		+	6.0	1.2×10^3

* At least $0.3 \mu\text{g m}^{-3}$ total mass in population.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Interactions: mixing
state, semivolatile
partitioning, and
coagulation**

J. Lu and F. M. Bowman

Table 5. Populations formed in external mixture simulation without coagulation.

Index	Composition					Mass ($\mu\text{g m}^{-3}$)	Number ($\# \text{ cm}^{-3}$)
	INERT	PO1	PO2	SV1	SV2		
1	+					30.0	9.8×10^4
2		+		+		12.1	2.4×10^4
3			+		+	14.2	2.4×10^4

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 6. Major populations* formed in external mixture simulations with different mixing criteria.

Index	Composition					Mass concentration ($\mu\text{g m}^{-3}$)			
	INERT	PO1	PO2	SV1	SV2	$c=0.02$	$c=0.05$	$c=0.1$	$c=0.2$
1	+					11.27	13.13	16.87	29.11
1a	+				+	0.05	0.10	0.05	0.33
2		+		+		0.16	3.03	3.57	6.37
2a		+		+	+	2.61	0.03	0.08	0.00
2b		+			+	0.00	0.00	0.00	0.37
3			+		+	3.04	3.51	4.10	7.09
4	+	+		+		5.27	8.28	9.41	6.57
4a	+	+				0.00	0.00	0.02	0.52
4b	+	+		+	+	2.01	0.87	1.07	0.00
5	+		+		+	7.54	9.35	12.94	7.29
6		+	+	+	+	0.88	0.93	0.85	–
6a		+	+		+	0.00	0.14	0.26	0.79
7	+	+	+	+	+	24.58	16.12	3.00	–
7a	+	+	+		+	0.85	2.72	5.97	0.00
All						0.00	0.02	0.04	0.03
Others									
Total mass						58.3	58.2	58.2	58.5

* At least $0.3 \mu\text{g m}^{-3}$ total mass in population for at least one mixing criteria.

Interactions: mixing state, semivolatile partitioning, and coagulation

J. Lu and F. M. Bowman

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

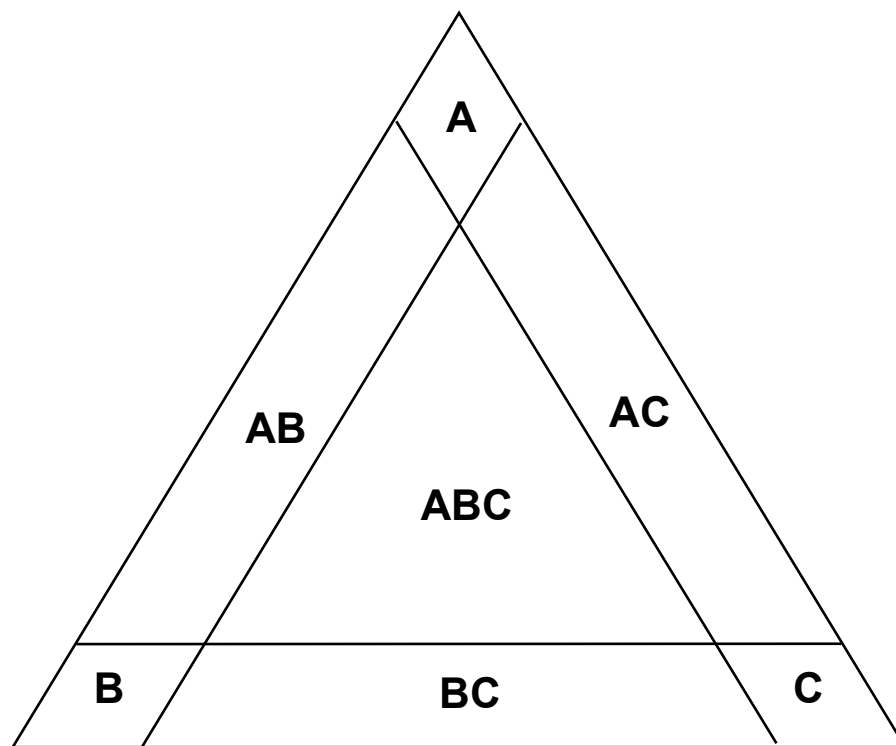
Printer-friendly Version

Interactive Discussion



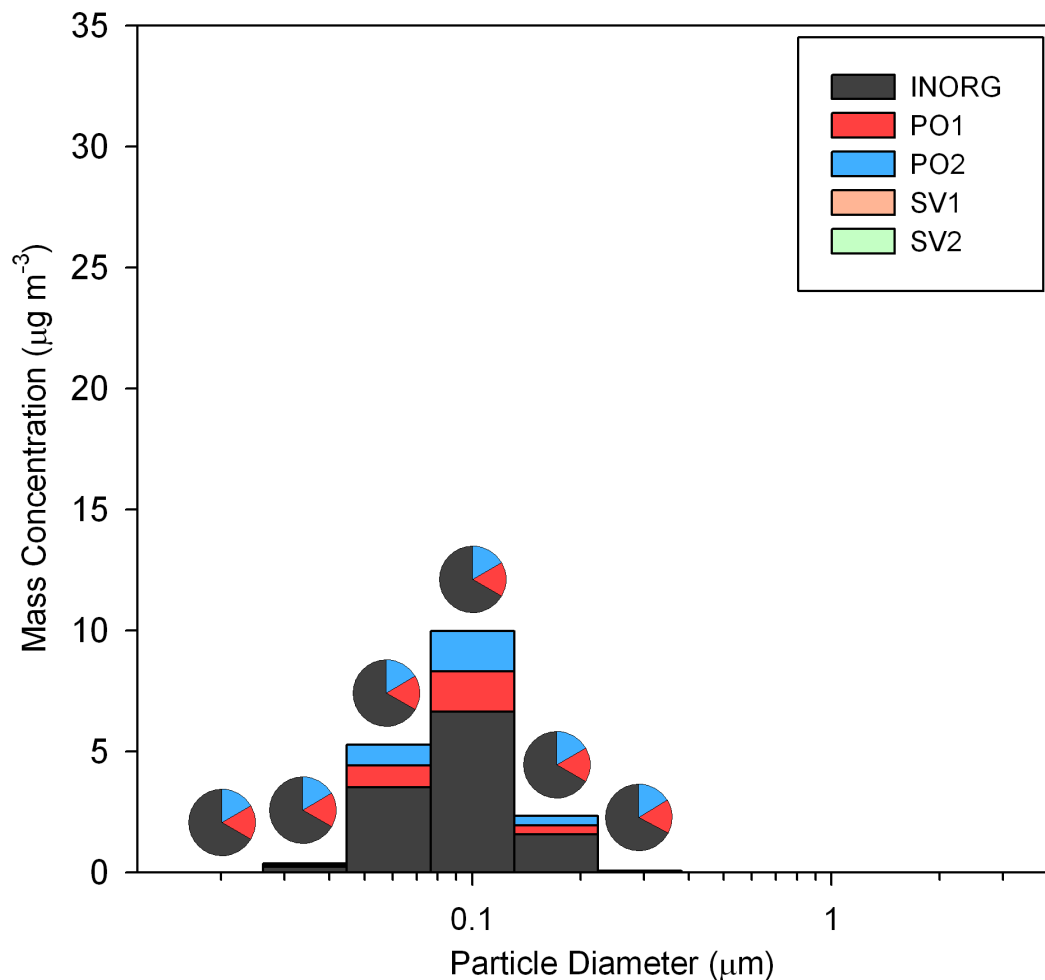
**Interactions: mixing
state, semivolatile
partitioning, and
coagulation**

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**Fig. 1.** Compositional categories for a ternary aerosol system.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Fig. 2.** Initial aerosol distribution for model simulations.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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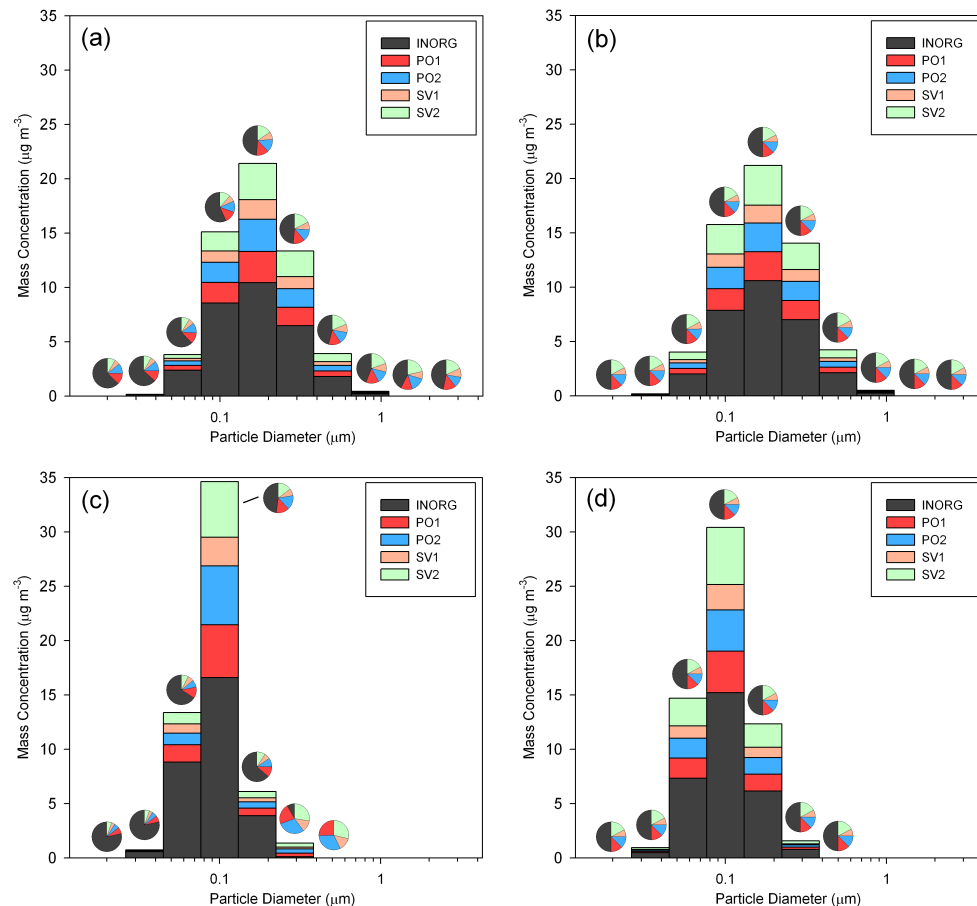


Fig. 3. Size and component distributions for base case scenario simulations. **(a)** external mixture with coagulation, **(b)** internal mixture with coagulation, **(c)** external mixture without coagulation, **(d)** internal mixture without coagulation.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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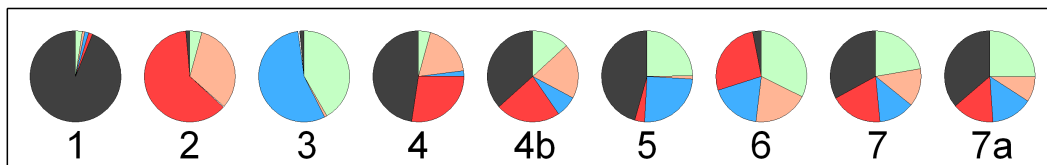
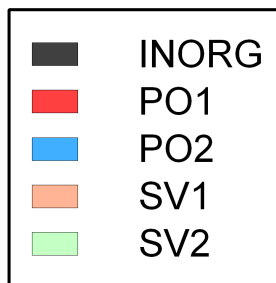
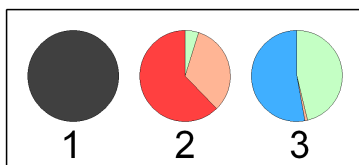
(a)**(b)**

Fig. 4. Compositional plots for external mixture aerosol populations formed in base case scenario simulations. **(a)** with coagulation, **(b)** without coagulation.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)