BLACK CARBON MIXING STATE IMPACTS ON AEROSOL ACTIVATION—
INVESTIGATIONS USING PARTICLE-RESOLVED MODEL SIMULATIONS

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Abstract

Black carbon-containing aerosol particles (called BC particles hereafter) are a major particle type in the atmosphere. Their source is the incomplete combustion of carbon containing material, which means that except for natural biomass burning all sources of BC particles are anthropogenic. They absorb solar radiation directly, warming the atmospheric layer where they reside. Because of the absorbing nature of BC particles and their relatively short life time compared to long-lived greenhouse gases (e.g. carbon dioxide), the reduction of BC emission has been suggested as a short-term global warming mitigation strategy. However, BC particles can also act as CCN, form cloud droplets and hence contribute to a cooling impact on climate. Both the optical properties and the CCN properties of BC particles depend on the BC mixing state, i.e. which other species are present within one BC-containing particle. The BC mixing state, in turn, evolves by so-called aerosol aging processes such as condensation of atmospheric gaseous components and coagulation with other aerosols. The climate effects of BC particles are therefore closely related to the BC mixing state and its evolution. Uncertainties regarding the representation of these processes in models are a major source of uncertainties in current climate model predictions. This dissertation focuses on studying the impact of mixing state of BC particles on cloud microphysical quantities during the early stages of cloud formation.

With the recently-developed particle-resolved model PartMC-MOSAIC, the mixing state and other physico-chemical properties of individual aerosol particles can be tracked as the particles undergo aerosol aging processes. As part of this dissertation this model framework was extended, and a particle-resolved cloud parcel model was developed. This simulates the
particle growth due to condensation of water vapor for each particle in a given population. The cloud parcel simulations are initialized with aerosol populations from urban plume simulations with PartMC-MOSAIC.

This new particle-resolved cloud parcel model was then used for quantifying the errors in computing cloud microphysical quantities due to simplified model representations of aerosol particles. A library of scenarios was designed by varying BC emission rates, background aerosol number concentrations and gas emission rates for the urban plume scenarios, and varying the cooling rate in the cloud parcel scenarios to explore how the errors depend on environmental conditions. In this analysis we focused on four cloud microphysical quantities, namely activation fraction, $f_N$, BC nucleation-scavenged mass fraction, $f_{BC}$, effective radius, $r_{eff}$, and dispersion, $\epsilon$, of the cloud droplet spectrum. The errors due to simplified mixing state representation for these quantities were largest when the population contained subpopulations of hydrophobic particles and hygroscopic particles. The errors in activation fraction $f_N$ was within 45%, while the error in $f_{BC}$ reached up to 1300% for these conditions. The errors in $r_{eff}$ and $\epsilon$ were within 12% and 62% respectively. An estimation of cloud short wave albedo revealed that the errors in effective radius led to a range of error in albedo between $-0.0055$ and $0.03$. For all quantities, the errors increased for the scenarios with reduced gas emission rates. For $f_{BC}$ decreasing errors were observed with increasing cooling rates, while for the other variables a dependence on cooling rate was not evident.

In addition to the development of modeling tools and the error quantification framework, this dissertation provided process analysis of how the change in aerosol population affected cloud droplet number concentration. A metric was developed to attribute the difference in cloud droplet number concentration, $N_d$ obtained (at the same cloud parcel cooling rate) between two particular environmental scenarios to the difference in aerosol population (called plume effect) and to the difference in water vapor competition (called parcel effect). For most of the scenarios presented, the plume effect dominated the parcel effect in changing $N_d$. Further, we investigated the kinetic limitation to cloud droplets growth. With the
use of the particle-resolved cloud parcel model, the types of kinetic limitation mechanisms affecting individual cloud droplets were revealed. Besides, applying the recently developed concept of chemical composition diversity by Riemer and West (2013), the relationship between chemical composition diversity of the aerosol population and the relative spectral dispersion of the cloud droplet spectrum were investigated. It is found that there is no strong association between chemically diverse aerosol populations and cloud droplet spectra with large dispersion. Instead cloud droplet number concentration and cooling rate are the key parameters controlling dispersion.
To my dearest parents
Acknowledgments

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Chapter 1

Introduction

1.1 Background and Motivation

1.1.1 Atmospheric aerosol and its relevance

An aerosol is defined as a suspension of solid or liquid particles in a fluid. In the case of atmospheric aerosols, the fluid is air. Aerosol particles can be of natural or of anthropogenic origin (Seinfeld and Pandis, 2006, Ch. 8.3, p. 381). They can be directly emitted, in which case they are called primary particles. Examples for primary aerosol particles include sea salt particles from the ocean, mineral dust particles from desert and roadside, pollen from plants, and combustion-generated particles directly emitted from vehicles and factories. They can also arise from the conversion of precursor gases (secondary particles). Secondary particles are for example sulfate particles that are formed in the exhaust of power plants or ships, as a result of the nucleation of sulfuric acid and water vapor.

Field observations show that aerosol populations exhibit broad size distributions, a diverse range of chemical compositions, as well as large spatial and temporal variability in the atmosphere. The size distribution can range from a few nanometers to hundreds of micrometers, spanning five order of magnitudes (Seinfeld and Pandis, 2006, Ch. 8.1, p. 350). Individual aerosol particles can be a complex mixture of a wide variety of species, such as soluble inorganic salts and acids, insoluble crustal materials (dust), trace metals, and car-
bonaceous materials. This reflects differences in their sources and history during transport in the atmosphere (Furutani et al., 2008; Murphy et al., 2007; Moffet et al., 2010) For example, Adachi and Buseck (2008) concluded from transmission electron microscope analyses that black carbon-containing particles are coated with organic matter and sulfates. Single particle analysis of biomass burning particles from the Las Conchas fire (New Mexico, 2011) using electron microscopy revealed the varying per-particle composition and morphology of this particle type (China et al., 2013). Lead is found in mixtures with biomass burning particles from wild fires and its amount can be quantified using single particle mass spectrometry (Murphy et al., 2007). Cluster analysis of aircraft-sampled aerosol particles using single-particle mass spectrometry showed that different particle classes can be identified, for example biomass burning particles mixed with sea salt and sulfates, and mixtures of organic compounds and sulfates (Zelenyuk et al., 2010).

A term that is often used in this context is the aerosol mixing state. In this dissertation, we use the term mixing state to describe how the aerosol chemical species are distributed amongst the particles of an aerosol population. Figure 1.1 shows an example of an aerosol population composed of two chemical species, with three different mixing states. A completely externally mixed population contains only particles of one species, while a completely internally mixed population contains identical particles which are a mixture of the two chemical species. Between those two extremes there are intermediate states possible, the center panel of Figure 1.1 showing one of them.

A more rigorous definition of mixing state was provided in Riemer and West (2013). Figure 1.2, adapted from Riemer and West (2013), illustrates the concept. The mixing state parameter, $\chi$, quantifies the degree to which an aerosol population is internally mixed. This parameter varies between 0% (completely external mixture) and 100% (completely internal mixture). As presented in Figure 1.2, $\chi$ is related to the average per-particle diversity of chemical species (as measured by $D_\alpha$) and the bulk population diversity (as measured by $D_\gamma$). A more detailed definition of $\chi$, $D_\alpha$ and $D_\gamma$, their meanings and applications are given
Atmospheric aerosol particles are of great concern since they affect air quality and threaten human health when they enter the human body through the respiratory tract (Pope and Dockery, 1996; Davidson et al., 2005; Pope and Dockery, 2006). In addition, aerosol particles are an important component in the Earth’s climate system. They affect climate system in a number of ways. First, aerosol particles absorb or scatter the incoming solar radiation, which is usually called the direct aerosol effect (McCormick and Ludwig, 1967; Charlson et al., 1992; Haywood and Boucher, 2000). This influences the amount of solar energy reaching the earth surface. Second, they can alter climate through modifying cloud microphysical properties, imposing indirect effects on the Earth climate system (Lohmann and Feichter, 2005). Aerosol particles participate in the cloud formation process as cloud condensation nuclei (CCN) or ice nuclei (IN) (Pruppacher and Klett, 1978). Specifically, Twomey (1974, 1977) suggested that an increased aerosol loading in the atmosphere will increase the cloud droplet number concentration, and, assuming constant liquid water content, reduce the cloud droplet size. This, consequently, enhances the cloud reflectivity reducing
Figure 1.2: Mixing state diagram illustrating the concepts of average per-particle diversity $D_\alpha$, bulk population diversity $D_\gamma$, and the mixing state parameter $\chi$. (Adapted from Riemer and West (2013))
the amount to solar energy reaching the Earth surface. This is called Twomey effect or first aerosol indirect effect. One of the remarkable examples of the first aerosol indirect effect is the the ship track phenomenon observed (Conover, 1966; Coakley et al., 1987; Ackerman et al., 2000). Further, with increased aerosol loading, the smaller size of the cloud droplets may cause less efficient collision and coalescence among cloud droplets. This, in turn, may decrease the production of precipitation, lengthen the life time of clouds and increase the cloud water content and cloud coverage. This is called Albrecht effect or second aerosol indirect effect (Albrecht, 1989).

A major source of current climate model predictions uncertainties continues to be due to uncertainties in aerosol effects (IPCC, 2001, 2007, 2013). The IPCC 2007 report revealed that the radiative forcing from the aerosol indirect effect is $-0.7 \text{ W m}^{-2}$ with the range between $-0.3 \text{ W m}^{-2}$ and $-1.8 \text{ W m}^{-2}$. The IPCC fifth assessment report (IPCC, 2013) revealed that the radiative forcing from the aerosol indirect effect is $-0.9 \text{ W m}^{-2}$ with the range between $-0.1 \text{ W m}^{-2}$ and $-1.9 \text{ W m}^{-2}$ (Figure 1.3). The radiative forcing of the aerosol effects on climate is the average values of a number of climate models and the uncertainty range represents the spread of all these model results. These uncertainties originate primarily from our limited understanding of various interactions, inaccurate representations or simplifications of aerosol physio-chemical properties and treatment of the physical and chemical processes in climate models (Zaveri et al., 2010). Ghan and Schwartz (2007) pointed out that to improve climate model predictions, more accurate representations of aerosol properties are essential. In short, reducing uncertainties in future climate predictions requires an improved understanding of physical and chemical processes of aerosols in the atmosphere, as well as better model representations of aerosol properties and processes. This dissertation contributes to the understanding of the effects of aerosol mixing state on cloud microphysical quantities and errors resulting from simplified mixing state representations.
Figure 1.3: The magnitudes of radiative forcing and their uncertainties imposed by some major components of both natural and anthropogenic sources on Earth climate system. (Adapted from IPCC fifth assessment report (IPCC, 2013, Ch. 8, Fig. 8.15).)
1.1.2 Black carbon-containing aerosols

Incomplete combustion of fossil fuels, biofuels and biomass produces carbonaceous particles, commonly called “soot” (Ramanathan and Carmichael, 2008). Soot is a complex mixture of so-called black carbon (BC) and organic carbon (OC) (Figure 1.4(b)) (United States Environmental Protection Agency, 2012). BC are agglomerations of small spherical elementary carbonaceous particles (Figure 1.4(a)). BC is a solid form of mostly pure carbon that absorbs solar radiation at all wavelengths (United States Environmental Protection Agency, 2012; Petzold et al., 2013). Organic carbon (OC) refers to the mix of compounds containing carbon bound with other elements like hydrogen or oxygen (United States Environmental Protection Agency, 2012; Petzold et al., 2013). The microstructure of BC is graphitic-like, containing a high fraction of sp\(^2\)-bonded carbon atoms. This explains the low chemical reactivity, and the strong optical absorption of BC (Petzold et al., 2013). BC is insoluble and experiences a slow removal by clouds and precipitation, unless it is coated with water-soluble compounds (Petzold et al., 2013). Several important properties of BC are summarized in Table 1.1, which is adapted from Petzold et al. (2013).

The properties of BC lead to numerous impacts on Earth climate system, affecting both global and regional climate (Cooke and Wilson, 1996; Ramanathan and Carmichael, 2008). Because of their absorbing nature, BC particles are called a “short-lived climate forcer” (Jacobson, 2002).

Beyond their direct interaction with radiation, BC particles existing near a cloud layer may promote cloud evaporation, this is usually referred as the semi-direct effect (Hansen et al., 1997; Ackerman et al., 2000). This cloud desiccation phenomenon has been observed during the INDOEX experiment over Indian Ocean (Ackerman et al., 2000) and in the Amazon Basin (Koren et al., 2004). Further, BC particles influence atmospheric dynamics (Menon et al., 2002), from local atmospheric stability (Koch and Genio, 2010) to large scale circulation (Hansen et al., 1997), which in turn impacts cloud formation, cloud cover and
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<td>Microstructure</td>
<td>graphitic-like structure containing a high reaction of sp²-bonded carbon atoms</td>
<td>low chemical reactivity in the atmosphere; slow removal by chemical processes; strong optical absorption</td>
</tr>
<tr>
<td>Morphology</td>
<td>aggregates consisting of small carbon spherules of &lt; 10 – 50 nm in diameter</td>
<td>high specific surface area; high capacity for sorption of other species</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>refractory material with a volatilization temperature near 4000 K; gasification is possible only by oxidation at T &gt; 340º C</td>
<td>high stability in the atmosphere; longer atmospheric life time</td>
</tr>
<tr>
<td>Solubility</td>
<td>insoluble in organic solvents including methanol and acetone, in water, and in the other components of atmospheric aerosol</td>
<td>slow removal by clouds and precipitation, unless coated with water-soluble compounds; longer atmospheric life time</td>
</tr>
<tr>
<td>Light absorption</td>
<td>uniformly absorbing in the VIS; characterized by a significant, non-zero and wavelength-independent imaginary part of the refractive index over VIS and NIR spectral regions</td>
<td>reduction of the albedo of clouds, snow, and ice; atmospheric heating; surface cooling - all of which lead to effects on solar radiation and climate</td>
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Table 1.1: Table “Properties defining Black Carbon” adapted from Petzold et al. (2013)
cloud microphysics (Ackerman et al., 2000), the hydrological cycle (Menon et al., 2002) and the Indian monsoon (Meehl et al., 2008). In addition, BC particles deposited on snow surfaces reduce the snow albedo. Consequently, the snow melting is accelerated and a snow albedo feedback can be triggered (Flanner et al., 2007).

The climate impacts of BC particles are complicated by the fact that their physicochemical properties evolve during their residence time in the atmosphere. BC particles are hydrophobic when freshly emitted (Weingartner et al., 1997), however their hygroscopicity change during transport in the atmosphere. They interact with other particles through coagulation, and with gaseous components through condensation. These processes are collectively known as aging, and change the per-particle chemical composition. As a result, BC particles become increasingly hydrophilic (Okada and Hitzenberger, 2001; Johnson et al., 2005; Moteki et al., 2007; Cubison et al., 2008). When the aged BC particles have high enough hygroscopicities, they can become cloud condensation nuclei (CCN), and contribute to the cloud droplet number concentration and the aerosol indirect effect.
In addition, the optical properties of aged BC particles change significantly compared to their freshly emitted counterparts. When other aerosol species form a coating on BC particles, the absorption of such internally mixed particles is enhanced (Jacobson, 2001; Bond et al., 2006). It has therefore been suggested that the reduction of BC particle emission may be a suitable short-term mitigation strategy to combat global warming (Jacobson, 2002, 2010; Chen et al., 2010; Bahadur et al., 2012). However, such reduction may potentially affect the BC contribution to the aerosol indirect effect (Chen et al., 2010) which implies a cooling.

Bond et al. (2013) provides a quantitative estimate of several primary climate forcings of BC parties and corresponding uncertainties, including direct effect, indirect effects on warm cloud, mixed phase and cold ice clouds. The authors in Bond et al. (2013) pointed out that the uncertainties are due to the insufficient understanding of the interactions between BC particles and clouds. In summary, BC particles exert several impacts on climate, and these impacts depend on the physico-chemical properties of the BC particles and their temporal evolution (Koch et al., 2011). There have been a number of modeling studies to simulate the aging process of black carbon aerosols in the atmosphere. These studies will be reviewed in the next subsection.

### 1.1.3 Modeling of BC aerosols aging

Since the BC climate impacts are so strongly tied to the BC mixing state, a substantial effort in both global and regional scale modeling exists to simulate the evolution of the mixing state of BC containing aerosol particles. Note that, in contrast, the aerosol representation in current cloud resolving models in general tends to be rather simplified. For example, some models predict CCN concentrations just based on background aerosol concentrations and environmental conditions, without considering chemical composition of the aerosol particles (Saleeby et al., 2010; Storer and van den Heever, 2012).

The earliest formulation implemented in global models is to track BC as two separate
populations, a hydrophobic population, representing fresh BC, and a hydrophilic population for aged BC. The conversion of BC from hydrophobic to hydrophilic is then modelled as an exponential decay with an aging time scale of about 24 h (Cooke et al., 1999; Lohmann et al., 1999). Obviously, this is a highly simplified treatment since the rate at which BC aging occurs depends on various environmental conditions. The atmospheric abundance and life time of BC particles are sensitive to the assumed time scale (Koch and Genio, 2010).

A more sophisticated approach than prescribing a fixed aging time scale is to simulate the evolution of physicochemical properties of aerosol populations by explicitly tracking interactions among a number of modes or distributions. In traditional aerosol models, the aerosol size distributions are either represented by a number of sections or modes (Figure 1.5). It then needs to be assumed that within one bin or mode all particles have the same composition (the “internal-mixture assumption”), which does not represent the reality of the aerosol particles found in the atmosphere.

The explicit tracking of intermodal and intersectional interactions require ad hoc rules to govern the transfer of mass between modes or sections (Wilson et al., 2001; Stier et al., 2005; Vignati et al., 2004). For example, Vignati et al. (2004) developed an aerosol module, in which aerosol populations are represented by seven modes. Intermodal and intramodal coagulations are not considered for coarse modes and accumulation insoluble mode. Bauer et al. (2008) designed an aerosol module which accepts a number of model configuration
options for implementing coagulation among particles. In a similar fashion, Riemer et al. (2003) implemented five modes in a mesoscale modal model. The five modes represent particles which are pure soot, internal mixture of soot with other species, and non-soot-containing. After intramodal coagulations, the particles are allocated in their original modes, while particles formed from intermodal coagulation would be put in the mode with larger median diameter. Similar rules have to be defined for condensation. Jacobson (2002) used 18 aerosol size distributions to represent the mixing state of the aerosol population. However, this more sophisticated treatment of aerosol mixing state evolution is still limited since particles for a certain class and size are assigned identical compositions.

Oshima et al. (2009) studied BC mixing state impacts on optical properties and CCN activities using a 2-dimensional bin structure to represent the size distribution, one dimension for BC core diameter and the second dimensions for BC mass fraction. In their study, the particle distribution is represented using 40 size bins and 10 BC dry mass fraction bins. While this approach allows a more detailed treatment of BC mixing state, it is impossible to generalize this method to represent the full mixing state of the population, since each species adds an additional dimension. For example, to resolve 20 model species using 40 size bins, a total of $40^{20}$ bins would be required to represent such a multidimensional distribution. The storage and computational cost scale exponentially with the number of species, making this approach computationally inhibitive. In contrast, for particle-resolved methods the storage and computational cost scale with the number of particles, not the dimension of the space that the particles are in.

In atmospheric sciences, particle-based methods have been used for investigating cloud microphysics. An explicit mixing cloud parcel model was developed to study how entrainment affects droplet spectral evolution (Krueger et al., 1997; Su et al., 1998), where droplet growth of individual droplets was considered. A particle-based model was developed by Shima et al. (2009) to study microphysical process in warm cloud, including condensation, evaporation, stochastic coalescence and sedimentation processes. However these atmospheric
applications of particle-based methods did not consider the coupling to aerosol chemistry processes and their effects on cloud microphysics.

The stochastic particle-resolved model PartMC-MOSAIC (Particle Monte Carlo-Model for Simulating Aerosol Interactions and Chemistry) was recently developed for atmospheric aerosol applications. PartMC simulates particle emissions, dilution with the background, and Brownian coagulation stochastically by generating a realization of a Poisson process. Gas- and aerosol-phase chemistry (including the gas-particle partitioning, calculation of activity coefficients, and intra-particle solid-liquid partitioning) are treated deterministically using the MOSAIC chemistry code (Zaveri et al., 2008). Since the individual particle composition is explicitly tracked, there is no need to invoke ad hoc aging criteria that move aerosol mass between bins or modes as is the case with traditional modal or sectional approaches described above. It also completely eliminates any errors associated with numerical diffusion, which is useful when investigating conditions where rapid condensation occurs. A brief technical description of PartMC-MOSAIC and relevant equations are included in Appendix G for reference.

1.2 Objectives

The climate impact of BC particles hinges on the evolution of the BC mixing state in the atmosphere by various processes, collectively known as aging. Representing these processes in models is challenging, and existing global and regional models handle the aging of black carbon aerosols in a highly simplified way. It is currently unclear what error is introduced by these simplifications.

This thesis focuses on one aspect of BC climate impacts, namely the role of BC particles as cloud condensation nuclei. The overarching research question is: What is the impact of BC mixing state on cloud microphysical quantities?

In answering this question, the contribution of this dissertation are threefold: (1) New
model development: The existing particle-resolved aerosol model PartMC-MOSAIC was further developed to simulate aerosol activation and subsequent condensational cloud droplet growth on a per-particle level. (2) Error quantification: A framework was established for quantifying the errors in computing cloud microphysical quantities due to simplified aerosol mixing state representations as they are used traditional models; and (3) Detailed process-level understanding: The relationships between aerosol mixing state, the growth of cloud droplets and cloud microphysical quantities were elucidated in detailed process studies.

1.3 Organization of thesis

Chapter 2 presents a description of the cloud parcel model development and the error quantification method. These tools are then applied to examine the impacts of BC mixing state on nucleation scavenging of BC, activation fraction of CCN, effective radius and relative spectral dispersion. This work was published as an article in the *Journal of Geophysical Research-Atmosphere*, with the title “Impacts of BC mixing state on BC nucleation scavenging: Insights from a particle-resolved model” (*Ching et al.*, 2012). Additional investigations on size-resolved BC nucleation fraction and kinetic limitation to cloud droplets growth, which are not part of the journal article, are included at the end of Chapter 2, before the conclusion of this chapter.

Chapter 3 is prepared as a journal article entitled “Impacts of BC particles mixing state on cloud microphysical properties: Sensitivity to environmental conditions”, to be submitted to *Journal of Geophysical Research-Atmosphere*. Here, the error quantification method developed in the previous chapter is applied to a wider range of environmental scenarios. Further, a process-level analysis is performed to attribute the difference in cloud droplet number concentration between any two scenarios to changes in the underlying aerosol population and to changes in the response of the maximum supersaturation in the cloud parcel. A new metric, the plume effect and the parcel effect, is introduced to quantify the
relative magnitude of these two factors.

In Chapter 4 we examine the relationship between aerosol mixing state and relative dispersion of cloud droplet spectrum. The chapter is prepared as a journal article entitled “Relationship between chemical diversity and relative spectral dispersion of a cloud droplet population” and to be submitted to *Journal of Geophysical Research-Atmosphere*. Chapter 5 summarizes the main findings of this dissertation, discusses its implications and proposes some future work. The Appendix lists the equations that were implemented to form the cloud parcel model, and provides a brief description of the PartMC-MOSAIC model.
Chapter 2

Impact of BC aerosol mixing state on cloud droplet formation and black carbon nucleation-scavenging

This chapter presents the model description of the particle-resolved cloud parcel model and illustrates how this framework is used to quantify the impacts of the mixing state of black carbon containing aerosol particles on four selected cloud microphysical target quantities. We focus on cloud droplet number concentration, the mass fraction of BC that is incorporated into cloud droplets, the effective radius, and the relative dispersion of the droplet size distribution. Most of the material of this chapter was published in the Journal of Geophysical Research (Ching et al., 2012). Subsection 2.7 and 2.8 present additional work that were not included in the publication Ching et al. (2012). In subsection 2.7, a qualitative comparison of modeled size-resolved black carbon nucleation fraction and observations of the same quantity taken on a mountain site by Schroder et al. (2011) is presented. Subsection 2.8 discusses the use of the particle-resolved model framework to investigate the kinetic limitation to the cloud droplets growth.

2.1 Introduction

Black-carbon-containing aerosol particles are important for regional and global climate (Forster et al., 2007). They both absorb and scatter light, thereby reducing the solar radiation at the Earth’s surface, and heating the atmosphere where they reside. Like other aerosol particles, black-carbon-containing particles can also serve as cloud condensation nu-
clei (Hitzenberger et al., 1999) or ice nuclei (DeMott et al., 1999; Möhler et al., 2005), and hence impact the cloud microphysical properties as well as the cloud lifetimes. Their ability to absorb radiation has several additional consequences regarding their interaction with clouds. When embedded in or near a cloud layer, black-carbon-containing aerosols may heat the layer and cause cloud evaporation (Hansen et al., 1997). Furthermore, they can impact the stability of the atmosphere and hence vertical motions, which, in turn, impact cloud development. Depending on the relative altitude of the black-carbon-containing particles and the cloud, their presence can lead to enhanced convection, causing a cloud increase, or suppression of cloud formation, causing a cloud reduction (Koch and Genio, 2010). These complex interplays contribute to the large uncertainties associated with the predictions of the net impact of black carbon mitigation (Chen et al., 2010; Spracklen et al., 2011; Bahadur et al., 2012).

Adding complexity is the fact that the optical properties and the cloud condensation nuclei and ice nuclei properties depend on the distribution of the per-particle composition of the black-carbon-containing aerosol, the so-called black carbon mixing state. Optical properties also depend crucially on the particle morphology and shape (Adachi et al., 2010). These properties in turn change continuously during the particles’ lifetime. Upon emission, the black carbon content and the presence of other constituents depend strongly on the type of source (Schwarz et al., 2008). In this work we focus on vehicle emissions from gasoline and diesel vehicles. Measurements show that the emitted particles from these sources are a complex mixture of many chemical species with the main constituents being black carbon and organic carbon (Medalia and Rivin, 1982; Toner et al., 2006), and trace concentrations of ionic and metallic species (Kleeman et al., 2000). During transport in the atmosphere, the particles’ compositions change further as a result of physical processes such as coagulation with other particles and condensation of secondary aerosol species, or as a result of chemical processes.

Along with these changes in composition, collectively termed “aging”, go changes in
both hygroscopicity and optical properties. Weingartner et al. (1997) concluded from their laboratory studies that freshly emitted combustion particles were unlikely to act as cloud condensation nuclei, whereas aging of the particles would improve their nucleation ability. Several recent field studies have confirmed this finding and show that the timescale of conversion from freshly emitted, hydrophobic black-carbon-containing particle to hydrophilic particle can be as low as a few hours during daytime (Wang et al., 2010; Moffet and Prather, 2009), consistent with modeling studies by Riemer et al. (2004) and Riemer et al. (2010).

Hence, to assess the budget of black carbon and its climate impact, it is important that regional and global models capture the evolution of the black carbon mixing state adequately (Croft et al., 2005). This is challenging, since, from a computational standpoint, resolving the mixing state ideally requires representing a multi-dimensional size distribution. Recently Riemer et al. (2009) developed PartMC-MOSAIC (Particle Monte Carlo-Model for Simulating Aerosol Interactions and Chemistry) for atmospheric aerosol applications. This stochastic particle-resolved model explicitly resolves the composition of individual aerosol particles in a given population of different particle types. Particle-based methods are efficient in resolving a multi-dimensional particle distribution as they scale with the number of particles, not with the number of dimensions.

PartMC simulates particle emissions, dilution with the background, and Brownian coagulation stochastically by generating a realization of a Poisson process. Gas- and aerosol-phase chemistry (including the gas-particle partitioning, calculation of activity coefficients, and intra-particle solid-liquid partitioning) are implemented deterministically by coupling with the MOSAIC chemistry code (Zaveri et al., 2008). Since individual particles are explicitly tracked, there is no need to invoke ad hoc aging criteria that move aerosol mass between bins or modes as is the case with traditional modal or sectional approaches (Riemer et al., 2003; Stier et al., 2005; Bauer et al., 2008; Jacobson, 2001). It also completely eliminates any errors associated with numerical diffusion, which is useful when investigating conditions where rapid condensation occurs.
In this work we extended the capabilities of PartMC-MOSAIC by adding a cloud parcel module, which allows competition between the aerosol particles for water vapor as the air parcel experiences cooling. With this model newly added cloud parcel module, we investigated the impacts of mixing state on cloud droplet formation. Throughout the past decades, cloud parcel models have been widely used for process studies to investigate the fundamentals relating to the drop size evolution and the factors that shape the cloud drop size spectrum (Howell, 1949; Mordy, 1959; Lee et al., 1980; Nenes et al., 2001; Conant et al., 2004). They have also been applied to investigate the interplay of cloud microphysics and chemistry (Nenes et al., 2002; Kreidenweis et al., 2003; Ervens et al., 2005) and to derive parameterizations for larger scale models (Ghan et al., 1993, 1995; Abdul-Razzak et al., 1998; Abdul-Razzak and Ghan, 2000; Nenes and Seinfeld, 2003; Fountoukis and Nenes, 2005; Segal and Khain, 2006; Ming et al., 2006).

The contribution of this work is that the cloud parcel model is initialized with an aerosol population where the mixing state is fully resolved on a per-particle basis. It therefore simulates the competition of the particles for water vapor without any simplifying assumption about composition, and the numerical solution is not subject to numerical diffusion. As shown in this work, this model framework can then be used to systematically quantify the importance of black carbon mixing state for cloud droplet formation, contrasting the importance of size information versus the importance of composition information.

Section 2.2 introduces the model system and the associated numerical methods. The setup of the simulations used in this chapter is described in Section 2.3. Section 2.4 presents the idealized plume scenario that served as a initialization for the cloud parcel simulations, which are described in Section 2.5. The simulation results are then used in Section 2.6 to quantify the importance of mixing state on cloud formation. Finally, we summarize our findings in Section 2.9.
2.2 Model description

2.2.1 The particle-resolved model PartMC-MOSAIC

The governing model equations and the numerical algorithms of the particle-resolved model PartMC-MOSAIC are described in detail in Riemer et al. (2009). Here we give a brief summary. In this work we used PartMC version 2.1.0 and MOSAIC version 2011-01-10.

We consider a Lagrangian parcel with volume $V_{\text{comp}}$, also called the computational volume. We represent the aerosol population by storing $N_p$ particles that reside in this volume, written $\Pi = (\vec{v}_1, \vec{v}_2, \ldots, \vec{v}_{N_p})$, where the particle order is not significant. Each particle is an $A$-dimensional vector $\vec{v}_i \in \mathbb{R}^A$ with components $(v^1_i, v^2_i, \ldots, v^A_i)$, so $v^a_i$ is the volume of species $a$ in particle $i$, for $a = 1, \ldots, A$ and $i = 1, \ldots, N_p$.

The simulation proceeds by two mechanisms. First, the composition of each particle can change, changing the components of the vector $\vec{v}_i$ for particle $i$ as species condense from the gas phase and evaporate to it. In this work, gas-phase chemistry and gas-particle partitioning, calculation of activity coefficients, and intra-particle solid-liquid partitioning are treated deterministically by the MOSAIC model (Zaveri et al., 2008). The current version of MOSAIC treats all the locally and globally important gas phase and aerosol species. The gas phase photochemical mechanism used is the carbon bond mechanism CBM-Z (Zaveri and Peters, 1999), which includes 77 model species and 142 reactions. The aerosol species include SO$_4$, NO$_3$, Cl, CO$_3$, MSA (methanesulfonic acid), NH$_4$, Na, Ca, other inorganic mass (which includes species such as SiO$_2$, metal oxides, and other unmeasured or unknown inorganic species present in aerosols), black carbon (BC), primary organic aerosol (POA), and secondary organic aerosol (SOA). Three computationally efficient modules are used in conjunction with CBM-Z, (1) the Multicomponent Taylor Expansion Method (MTEM) for estimating activity coefficients of electrolytes and ions in aqueous solutions (Zaveri et al., 2005b); (2) the Multicomponent Equilibrium Solver for Aerosols (MESA) for intraparticle solid-liquid partitioning (Zaveri et al., 2005a); and (3) the Adaptive Step Time-split Euler
Method (ASTEM) for dynamic gas-particle partitioning over size- and composition-resolved aerosol (Zaveri et al., 2008). SOA is treated based on the Secondary Organic Aerosol Model (SORGAM) scheme (Schell et al., 2001) and represented by four model species originating from the oxidation of anthropogenic VOC precursors (ARO1, ARO2, ALK1, OLE1), and four model species from the oxidation of biogenic VOC precursors (LIM1, LIM2, API1, API2).

Second, the particle population Π can have particles added and removed, either by emissions, dilution or coagulation events between particles. While condensation/evaporation is handled deterministically, the efficient stochastic PartMC model (Riemer et al., 2009) is used for emission, dilution, entrainment, and Brownian coagulation. In this work PartMC explicitly represented every aerosol particle in the volume $V_{\text{comp}}$, corresponding to an unweighted simulation in the sense of DeVille et al. (2011).

### 2.2.2 Cloud parcel model

In this section we describe the coupling of PartMC-MOSAIC with a cloud parcel model. To focus our simulations on the impacts of mixing state, we do not include any entrainment into the cloud parcel. Additionally, surface tension effects on droplet growth, sedimentation, and coagulation in the cloud parcel are not included.

The system of ordinary differential equations that is solved for the cloud parcel is derived using classical Köhler theory (Köhler, 1936; Seinfeld and Pandis, 1997) adapted to the $\kappa$ hygroscopicity parameterization (Petters and Kreidenweis, 2007). The state of the system is described by the prognostic variables $(S_v, D_1, \ldots, D_{N_p})$, where $S_v$ is the environmental saturation ratio and $D_i$ is the wet diameter of particle $i$, giving $N_p + 1$ variables in total. There are thus $N_p + 1$ corresponding differential equations, consisting of the condensational growth equation for each individual particle and the equation for the rate of change of environmental saturation ratio $S_v$.

During the cloud parcel simulation, the constituent volumes $v_i^a$ of each particle $i$ are
held fixed for each species $a$ except water. We number the species so that water is the $A$th species, and we write $v_i^w = v_i^A$ for the water volume in particle $i$. This varies with the wet diameter $D_i$ according to

$$v_i^w = v_i - v_i^{\text{dry}},$$

where $v_i = \frac{\pi}{6}(D_i)^3$ is the total volume and $v_i^{\text{dry}}$ is the dry volume, obtained by summing the constituent species volumes over all non-water species, so that

$$v_i^{\text{dry}} = \sum_{i=1}^{A-1} v_i^a.$$  

We will use these volumes below in the mixing rule assumptions for hygroscopicity parameters, as in Petters and Kreidenweis (2007).

The condensational growth rate $\dot{D}_i$ of aerosol particle $i$ is given by the solution to the pair of implicit equations:

$$\dot{D}_i = \frac{4D_{v,i}M_wP^0}{\rho_wRTD_i} \left( S_v - a_{w,i} \frac{1}{1 + \delta_i} \right) \times \exp \left( \frac{4M_w\sigma_w}{\rho_wRTD_i} \frac{1}{1 + \delta_i} + \frac{\Delta H_v M_w}{RT} \frac{\delta_i}{1 + \delta_i} \right),$$

$$\delta_i = \frac{\Delta H_v \rho_w}{4k'_{a,i}T} D_i \dot{D}_i.$$  

See Seinfeld and Pandis (1997) for a comprehensive derivation of these and other equations. Here, $D_{v,i}$ is the corrected diffusivity coefficient for particle $i$, $a_{w,i}$ is the water activity of particle $i$, $\sigma_w$ is the water surface tension, $\Delta H_v$ is the specific latent heat of vaporization of water, $k'_{a,i}$ is the corrected thermal conductivity of air for particle $i$, $T$ is the environmental temperature, $\rho_w$ is the density of water, $M_w$ is the molecular weight of water, $R$ is the universal gas constant, and $P^0$ is the saturation vapor pressure. The formulations for $D_{v,i}$, $k'_{a,i}$, and $P^0$ used here are given in Appendix A.1.
We express the water activity $a_{w,i}$ in equation (2.3) in terms of a dimensionless hygroscopicity parameter as was suggested by Ghan et al. (2001) and Petters and Kreidenweis (2007). The latter authors termed this parameter $\kappa$, and we adopt this notation. The water activity is then given by

$$ a_{w,i} = \frac{v_{w,i}^{w}}{v_{i}^{w} + \kappa_{i}v_{i}^{\text{dry}}}. \quad (2.5) $$

For an aerosol particle $i$ containing several non-water species, the $\kappa_{i}$ value for the particle is the volume-weighted mean of the individual $\kappa^{a}$ of each constituent species $a$ (Petters and Kreidenweis, 2007), so

$$ \kappa_{i} = \frac{A^{-1}}{\sum_{a=1}^{A} \kappa^{a}v_{i}^{a}}v_{i}^{\text{dry}}, \quad (2.6) $$

where the sum is over all non-water species (recalling that water is the $A$th species). Following Petters and Kreidenweis (2007) and Riemer et al. (2010), we assumed $\kappa = 0.65$ for all salts formed from the $\text{NH}_4^+ - \text{SO}_4^{2-} - \text{NO}_3^-$ system. For all MOSAIC model species that represent secondary organic aerosol (SOA) we assumed $\kappa = 0.1$, based on measurements by Prenni et al. (2007). Following Petters et al. (2006) we assumed $\kappa = 0.001$ for primary organic aerosol (POA) and $\kappa = 0$ for black carbon (BC). We do not consider sparingly soluble species (Petters and Kreidenweis, 2008) in this work. See Appendix A.2 for a discussion of why constant $\kappa$ values were assumed.

The rate of change of the environmental saturation ratio, $\dot{S}_{v}$, is the sum of the rate due to each particle and the rate due to temperature changes in the environment, giving

$$ \dot{S}_{v} = -\sum_{i=1}^{N_{p}} \frac{\pi \rho_{w}RT}{2M_{w}P_{0}V_{\text{comp}}} D_{i}^{2}\dot{D}_{i} - \frac{1}{P_{0}} \frac{\partial P_{0}}{\partial T} S_{v}\dot{T}, \quad (2.7) $$

where $\dot{T}$ is the prescribed rate-of-change of the temperature and we assume that the pressure is held constant. The modeling approach used here follows Majeed and Wexler (2001) in prescribing the cooling rate. An alternative modeling framework would prescribe the updraft velocity and compute the temperature change. However, computing temperature changes
would require the modeling of radiative heating effects (Conant et al., 2002), which would significantly complicate the interpretation of our results. The pressure is kept constant for simplicity, following Majeed and Wexler (2001), as detailed reproduction of the updraft process is not relevant for this study.

Here the computational volume, \( V_{\text{comp}} \), starts at the initial value \( V_{\text{comp}}^0 \) and varies with environmental temperature as described by the law for ideal gases.

The evolution of the water condensation dynamics is defined by equations (2.3), (2.4), and (2.7). In PartMC-MOSAIC these equations are solved numerically as described in Appendix A.3.

### 2.2.3 Critical diameter and critical saturation

In the following, we will frequently refer to the critical diameter and the critical supersaturation for the aerosol particles. To define these, we first find the equilibrium saturation ratio, \( S_{e,i} \), for particle \( i \) by setting \( \dot{D}_i = 0 \) in (2.3) and (2.4). This gives

\[
S_{e,i} = a_{\text{w},i} \exp \left( \frac{4M_w \sigma_w}{RT \rho_w D_i} \right). \tag{2.8}
\]

The critical diameter, \( D_{c,i} \), for particle \( i \) is the diameter that maximizes the equilibrium saturation ratio, and will be the unique solution of

\[
\frac{\partial S_{e,i}}{\partial D_i} \bigg|_{D_i = D_{c,i}} = 0. \tag{2.9}
\]

The critical saturation ratio, \( S_{c,i} \), for particle \( i \) can then be found by evaluating the equilibrium saturation ratio (2.8) at the critical diameter, giving

\[
S_{c,i} = S_{e,i} \big|_{D_i = D_{c,i}}. \tag{2.10}
\]
The critical supersaturation is then defined as

\[ s_{c,i} = S_{c,i} - 1. \]  

(2.11)

### 2.3 Description of simulations

The simulations in this work were performed in a two-stage process. First, we simulated a single Lagrangian parcel moving over a polluted urban environment for 48 h, which we call **plume time** \( t_p \) (see Section 2.4.1). Second, we took snapshots of the aerosol population at each hour (giving 49 snapshots in total) and used these as input for 49 separate cloud parcel simulations, each lasting for 10 min of **cloud parcel time** \( t_c \) (see Section 2.5). The cloud parcel simulations do not feed back into the urban plume simulation. Instead, they are used to accurately compute and compare the process of cloud droplet formation and growth for underlying aerosol populations that have experienced different degrees of aging.

The urban plume simulation includes a number of aerosol processes that are treated stochastically, i.e. the dilution, emission, and Brownian coagulation of aerosol particles. To obtain statistically robust results we produced an ensemble of urban plume simulations with subsequent (strictly deterministic) cloud parcel simulations and averaged the results over the ensemble. Each member run of the ensemble consists of approximately 10 000 computational particles. The 95% confidence interval based on the 10 members is a small fraction of the mean during the 2-day simulation. For example, the 95% confidence interval for activation fraction ranges between 0.4% and 1.3% of its mean. Based on the 95% confidence interval, we concluded that an ensemble of ten 10 000-computational particle members is sufficient to obtain a statistically robust result. The figures in the result sections show the 10-member ensemble averages along with the 95% confidence intervals unless stated otherwise.
2.4 Urban plume simulation

2.4.1 Urban plume simulation setup

For this study we use the urban plume case as described in Zaveri et al. (2010), which simulates an aerosol population undergoing emissions, dilution, Brownian coagulation, and gas and aerosol chemistry for 48 h of plume time, \( t_p \). See Zaveri et al. (2010) for a detailed analysis of these simulation results. Here we summarize this simulation as it pertains to the discussion of the cloud parcel results. The simulation was run with approximately \( N_p = 10,000 \) simulated particles, with the exact number of particles varying over the course of the simulated period. The time step for the urban plume simulations was 60 seconds.

For this scenario we assumed that an air parcel containing background air was advected within the mixed layer across a large urban area. While traveling over the urban area in the first 12 h, the air parcel was exposed to continuous emissions of NO\(_x\), SO\(_2\), CO, volatile organic compounds (VOCs), and primary aerosol particles of three different types, namely diesel soot (70% black carbon (BC) + 30% primary organic aerosol (POA)), gasoline soot (20% BC + 80% POA), and meat cooking primary organic aerosol (100% POA). Table 2.1 lists the details for the initial and emitted aerosol size distribution parameters.

While the cloud parcel simulations did not include any entrainment as described in Section 2.2.2, the urban plume air parcel did experience dilution due to vertical entrainment of background air during the first 6 h as the mixed layer continued to grow, and continuous dilution with background air due to horizontal dispersion. The latter was modeled as a first order process, assuming a dilution rate of 5.4% h\(^{-1}\). The background air was composed of 50 ppbv O\(_3\) and low concentrations of other trace gases. It also contained background aerosol consisting of ammonium sulfate and secondary organic aerosol with trace amounts of black carbon in internal mixture.

The temperature was prescribed along the trajectory, as shown in Figure 2.1a. For simplicity we assumed that the temperature stayed constant after the first 6 h. This is
Initial/Background

<table>
<thead>
<tr>
<th>Mode</th>
<th>$N_a$ / cm$^{-3}$</th>
<th>$D_g$ / $\mu$m</th>
<th>$\sigma_g$</th>
<th>Composition by mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aitken mode</td>
<td>1800</td>
<td>0.02</td>
<td>1.45</td>
<td>49.64% (NH$_4$)$_2$SO$_4$ + 49.64% SOA + 0.72% BC</td>
</tr>
<tr>
<td>Accumulation mode</td>
<td>1500</td>
<td>0.116</td>
<td>1.65</td>
<td>49.64% (NH$_4$)$_2$SO$_4$ + 49.64% SOA + 0.72% BC</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Emission</th>
<th>$E_a$ / m$^{-2}$ s$^{-1}$</th>
<th>$D_g$ / $\mu$m</th>
<th>$\sigma_g$</th>
<th>Composition by mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meat cooking</td>
<td>$9 \times 10^6$</td>
<td>0.086</td>
<td>1.91</td>
<td>100% POA</td>
</tr>
<tr>
<td>Diesel Vehicles</td>
<td>$1.6 \times 10^8$</td>
<td>0.05</td>
<td>1.74</td>
<td>30% POA + 70% BC</td>
</tr>
<tr>
<td>Gasoline Vehicles</td>
<td>$5 \times 10^7$</td>
<td>0.05</td>
<td>1.74</td>
<td>80% POA + 20% BC</td>
</tr>
</tbody>
</table>

Table 2.1: Area source strength, $E_a$, of the three types of emission and the initial/background aerosol population. The initial/background aerosol population size distribution is assumed to be lognormal and defined by the number concentration, $N_a$, the geometric mean diameter, $D_g$, and the geometric standard deviation, $\sigma_g$.

consistent with the idea that the air parcel remained in the fully mature mixed layer or the residual layer thereafter. The total water content of the air was assumed to be constant along the trajectory, so the saturation ratio varied as shown in Figure 2.1a.

### 2.4.2 Urban plume simulation results

Figure 2.1b–d show the evolution of the total aerosol number concentration and bulk aerosol mass concentration of the major aerosol species, respectively, in the air parcel traveling with the plume. The particle number concentration $N_a$ increased initially due to the emission of primary particles and reached a maximum of 15 000 cm$^{-3}$ at $t_p = 12$ h. After $t_p = 12$ h, $N_a$ decreased because the emissions were switched off, and dilution and coagulation reduced the particle number concentration. Similarly, the BC and POA mass concentration increased for the first 12 h due to emission, and decreased thereafter due to dilution with the background. The time series of the secondary aerosol species sulfate and SOA were determined by the interplay between loss by dilution and photochemical production. The ammonium nitrate mass concentration depended on the gas concentrations of its precursors, HNO$_3$ and NH$_3$. 
Figure 2.1: (a) Prescribed temperature $T$ and calculated saturation ratio $S_v$ over the course of the two-day urban plume simulation, (b) evolution of total particle number concentration $N_a$ and geometric mean diameter of the dry aerosol particle population $D_g$, (c) and (d) evolution of key bulk aerosol species. The results from this simulation serve as input data for the cloud parcel model.
When the two gas precursors were abundant during the first 12 h, ammonium nitrate formed rapidly. After this, HNO$_3$ and NH$_3$ decreased due to dilution, and the ammonium nitrate evaporated. Figure 2.1b shows the geometric mean diameter of the particle population, which increased from about 50 nm to 100 nm over the course of the first day due to the condensation of secondary species.

To characterize the black carbon mixing state, we define the per-particle BC mass fraction in particle $i$ as

$$w_{BC,dry,i} = \frac{\mu_{BC,i}}{\mu_{dry,i}} \quad (2.12)$$

where $\mu_{BC,i}$ is the mass of BC in particle $i$ and $\mu_{dry,i}$ is the total dry mass of the particle (non-water mass). We then define a two-dimensional number concentration that is a function of both diameter and BC mass fraction. The two-dimensional cumulative number distribution $N(D,w)$ is the number of particles per volume that have a diameter less than $D$ and a BC mass fraction less than $w$. The two-dimensional number distribution $n(D,w)$ is then defined by

$$n(D,w) = \frac{\partial^2 N(D,w)}{\partial \log_{10} D \partial w}. \quad (2.13)$$

Figure 2.2 shows the two-dimensional number concentration distribution of the particles as a function of dry diameter and BC dry mass fraction, $n(D_{dry}, w_{BC,dry})$, after 1, 7, 15, and 36 h of simulation. This corresponds to local standard times 0700, 1300, 2100, and 1800 on the next day.

At $t_p = 1 \text{ h}$ (Figure 2.2a) three major types of particles could be distinguished. They corresponded to the meat cooking emissions and background particles ($w_{BC,dry} = 0\%$ and $w_{BC,dry} = 0.72\%$, respectively), gasoline vehicle emissions ($w_{BC,dry} = 20\%$), and diesel vehicle emissions ($w_{BC,dry} = 70\%$). Some particles existed with intermediate values for $w_{BC,dry}$. They were the result of the formation of secondary aerosol species condensing onto the particles and coagulation among particles, thereby changing $w_{BC,dry}$ over time.
At $t_p = 7$ h (Figure 2.2b) a continuum of black carbon mixing states had developed as a result of continued fresh emissions on the one hand and the subsequent aging of those particles due to coagulation and condensation on the other hand. Most particles had a black carbon mass fraction between 0% and 30%. The diagonal lines appeared due to the fact that as condensation was ongoing, the BC mass fraction of small particles decreased faster than that of large particles.

At $t_p = 12$ h emissions were switched off, and from that time onwards diesel emission particles with $w_{BC,dry} = 70\%$ were no longer replenished. This is evident in the graph for $t_p = 15$ h (Figure 2.2c) where the maximum BC mass fraction had decreased to 60%. Concurrently the small BC containing particles were depleted by coagulation with larger particles. This continued for the remainder of the simulation so that at $t_p = 36$ h (Figure 2.2d) most particles had a BC mass fraction lower than 40%. The particles smaller than 0.04 $\mu$m are background particles that continued to enter the parcel by dilution. It should be noted that the mass fractions of species other than BC also changed, and hence the aerosol mixing state with respect to other species, but we do not include these figures here for brevity.

Similarly to $w_{BC,dry}$ we can use the hygroscopicity parameter $\kappa$ to define a two-dimensional number concentration distribution $n(D, \kappa)$. The result is shown in Figure 2.3, which displays the particle population at the same points in time as Figure 2.2. Figure 2.3a shows three sub-populations for $t_p = 1$ h. The sub-population at $\kappa \approx 0$ represents the freshly-emitted BC-containing particles (diesel and gasoline) as well as the particles originating from meat cooking. The sub-population at $\kappa \approx 0.4$ consists of background particles that contained a mixture of ammonium sulfate and biogenic SOA (see Table 3.1). The double-banded structure can be explained by differing nitrate contents owing to the timing when the particles entered the plume and the resulting impact on water uptake and nitrate formation. Particles that were present at $t_p = 0$ or that were diluted in shortly after contained water because the saturation ratio $S_v$ was above the deliquescence point (see Figure 2.1a). These particles were able to acquire nitrate, which raised their $\kappa$-value slightly. During the simulation $S_v$ in
Figure 2.2: Two-dimensional number concentration distribution $n(D_{dry}, w_{BC,dry})$ at (a) $t_p = 1$ h, (b) 7 h, (c) 15 h, and (d) 36 h.
the plume decreased, and particles that entered the simulation after $S_v$ dropped below the deliquescence point, remained dry. Nitrate formation was not possible on these particles in the first few hours of simulation because the HNO$_3$ mixing ratio was still too low. These particles form the band at $\kappa = 0.34$. We observe a third band around $\kappa \approx 0.6$. These are background particles that lost their biogenic SOA material due to evaporation.

As the aerosol particles were processed in the plume and condensation of inorganic and organic semivolatile species occurred as well as coagulation these structures changed accordingly. At $t_p = 7$ h a continuous range of $\kappa$ values was established as very freshly emitted BC-containing particles coexisted with particles that had experienced aging of different degrees. At this plume time all particles contained some SOA, which explains why $\kappa$ was less than 0.6 for all particles. After emissions stopped, particles with $\kappa \approx 0$ were not replenished.
anymore and the clusters of particles moved along the $\kappa$-axis to larger values. Background particles were continuously diluted in as already seen in Figure 2.2. Given the temperature of the air parcel and the concentration level of biogenic SOA precursor, their SOA material evaporated, and they show as a line at $\kappa = 0.65$.

Figure 2.4 shows the two-dimensional number concentration distribution as a function of the dry diameter and critical supersaturation, $n(D_{\text{dry}}, s_c)$, at the same times as in Figure 2.2 and 2.3. As expected from Köhler theory, the larger the size of the particle, the lower is the critical supersaturation. However, size is not the only parameter determining critical supersaturation. At a given size the particles can have different critical supersaturation values due to differences in their compositions. For example at $t_p = 1$ h, particles with size of 0.1 $\mu$m had $s_c$ ranging from 0.1% to 2%. At $t_p = 1$ h, the two maxima of the 2-D distribution, $n(D_{\text{dry}}, s_c)$ corresponded to gasoline and diesel particles (low $\kappa$) and to background particles (high $\kappa$).

As the simulation time proceeded, an increasing number of particles became more hygroscopic, and the maximum of the number concentration distribution moved to lower $s_c$ values. However since during the emission phase fresh emissions were continuously supplied, the spread of the distribution with respect to $s_c$ was maintained. Only after emissions were turned off, the distribution with respect to $s_c$ became narrower meaning that the aerosol distribution moved towards an “internally mixed” state with respect to CCN properties. This is apparent in the graph for $t_p = 36$ h.

Figure 2.4 is consistent with the findings by Dusek et al. (2006b), often loosely paraphrased as “size matters more than composition”. It shows that resolving size is imperative for predicting CCN properties as it is the dominant factor in determining critical supersaturation. Differences in composition modulate this relationship by causing some spread of $n(D_{\text{dry}}, s_c)$ in the $s_c$-dimension. This spread tends to be large when particles of very different hygroscopic properties are present. There are various circumstances that can lead to such conditions. In our simulations this is the case at early plume times, when background
Figure 2.4: Two-dimensional number concentration distribution $n(D_{\text{dry}}, s_c)$, at (a) $t_p = 1$ h, (b) 7 h, (c) 15 h, and (d) 36 h.
particles coexist with freshly emitted BC-containing particles. Further, this spread is also maintained when fresh emissions enter the air parcel, and at the same time efficient aging mechanisms are operating, as occurs during the daytime in our simulations. When emissions stop, but aging mechanisms are still at work, the aerosol population moves towards an internal mixture with respect to CCN properties, and consequently the spread in $s_c$-dimension becomes smaller, as can be seen on the second day of our simulations.

2.5 Cloud parcel simulation

2.5.1 Cloud parcel simulation setup

Each cloud parcel simulation was initialized with the aerosol population taken from a specific point along the urban plume trajectory, corresponding to a particular plume time, $t_p$. The cloud parcel model simulations started at a saturation ratio of $S_v = 95\%$ and a temperature of $T = 290$ K, and the particle population had the initial per-particle water content $v_{i, w}$ adjusted so that each particle was at equilibrium (i.e., so that $S_{e, i} = 95\%$ in (2.8)). The time step for the cloud parcel simulations was 1 second.

For the base case the cloud parcel model was then run for 10 min of cloud parcel time, $t_c$, with a constant temperature decrease of 0.5 K/min prescribed throughout the 10 min simulation and constant pressure. This cooling rate can be approximately interpreted as modeling an air parcel with an updraft velocity on the order of 0.85 m/s (assuming subsaturated, double this velocity for supersaturated). Since previous studies showed a profound impact of the cooling rate on CDNC (Feingold, 2003), we performed two additional sets of cloud parcel simulations, one set with a cooling rate of 0.25 K/min and one set with 1 K/min.
2.5.2 Cloud parcel simulation results

We used the particle-resolved aerosol population output from the urban plume simulation at every hour as input to the cloud parcel model as described in Section 2.2.2. As shown in Figures 2.1 and 2.2 these particle populations represented urban, polluted conditions where the bulk concentrations as well as the mixing state varied from hour to hour.

Figure 2.5 shows an example for the time series of temperature and saturation ratio as a function of cloud parcel time $t_c$. Here we used the aerosol distribution at plume time $t_p = 15$ h as input and the cooling rate of 0.5 K/min. The evolution of the saturation ratio was the result of the interplay of the prescribed cooling rate and the loss of water vapor due to condensation on the particles according to Equation (2.7). In this example a maximum saturation ratio of $S_{\text{max}} = 100.22\%$ was reached at $t_c = 1.75$ min.

Figure 2.6 shows the corresponding particle and droplet number size distribution as a function of wet diameter, $n(D_{\text{wet}})$, at $t_c = 0$ min (red), 2 min (blue), 10 min (green). The spectrum at $t_c = 0$ min is the aerosol distribution at $t_p = 15$ h. At $t_c = 2$ min, aerosol activation had occurred and the spectrum had become bimodal. The mode with the larger particles represents the cloud droplets with a mean wet diameter of $\bar{D} = 3.8 \ \mu\text{m}$ and a
relative dispersion of $\epsilon = 0.19$. Relative dispersion is defined as the ratio of the standard deviation of the size spectrum $\sigma(n(D))$ to the mean diameter $\bar{D}$, so that

$$
\epsilon = \frac{\sigma(n(D))}{\bar{D}}. 
$$

The mode with the smaller particles represents the interstitial aerosol. As the environmental relative humidity increased at the start of the simulation, these particles exhibited hygroscopic growth.

At $t_c = 10$ min, the interstitial population remained essentially unchanged compared to $t_c = 2$ min, while the cloud droplet distribution had further grown to a mean diameter of $\bar{D} = 10.9 \, \mu m$. The cloud droplet mode had also narrowed to $\epsilon = 0.10$. Note that the particle-resolved method does not suffer from numerical diffusion when calculating the rapid growth of the activated cloud droplets.

In this study we followed Cubison et al. (2008) and counted the particles that resided in the mode with larger sizes (i.e. $D_{\text{wet}} > 2 \, \mu m$) as cloud droplets. It is possible that amongst this droplet mode there were some particles that had a critical diameter larger than $2 \, \mu m$ and that this critical diameter was not reached during the simulation time. Those particles, although of similar sizes as the activated cloud drops, were then not yet activated. This
Figure 2.7: Maximum supersaturation, $s_{\text{max}}$, attained in the 10-min parcel simulations as a function of plume time $t_p$. The thin solid line (cooling rate of 0.5 K/min) shows the average of an ensemble of 10 simulations. The error bars represent the 95% confidence interval. The thick solid line (cooling rate of 1 K/min) and the dashed line (cooling rate of 0.25 K/min) represent one ensemble member.

"inertial effect" was described by Chuang et al. (1997) and Nenes et al. (2001). As detailed analysis of our model output revealed, most of the particles with critical diameter larger than 2 $\mu$m were indeed activated cloud droplets, i.e. they exceeded their critical diameters during the simulation time and continued to grow until the end of the simulation. Only very few of the droplets in our cloud parcel simulations were subject to the inertial effect.

In Figure 2.7 we mapped the resulting maximum supersaturations $s_{\text{max}}$ for the three sets of cloud parcel runs as a function of plume time $t_p$. For each set we used the same temperature profile for all cloud parcels, therefore the exact value for $s_{\text{max}}$ depended exclusively on the initial aerosol distribution. It ranged for the base case between 0.35% for cloud parcels that were initialized with the aerosol population at $t_p = 0$ h and 0.2% for cloud parcels that were initialized with aerosol populations around $t_p = 12$ h. As expected, low values of $s_{\text{max}}$ were reached when the cloud parcel simulations were initialized with aerosol populations that contained a large number of aerosol particles and that were able to activate to cloud droplets competing for water vapor.

For further analysis, we define the cloud droplet fraction, $f_N$, as the ratio of cloud droplet number concentration, $N_d$, to the total number concentration of particles, $N_a$. The
nucleation-scavenged mass concentration of BC is defined as the mass concentration of BC associated with the cloud droplets. The nucleation-scavenged mass fraction of BC, \( f_{\text{BC}} \), is then defined as the ratio of BC mass concentration that is associated with the cloud droplets to the total BC mass concentration.

Figure 2.8 shows the results of \( f_N \) and \( f_{\text{BC}} \) for the 49 cloud parcel simulations. The fraction of particles that became cloud droplets generally increased for cloud parcels initialized with particle populations from the later part of the 48-hour urban plume simulation. While during the morning of the first day \( f_N \) amounted to only 20%, this increased to about 70% by the end of the second day. This is consistent with the notion that the aerosol population during the early plume hours contained a large proportion of “fresh” BC containing particles, which were not easily activated. Over the course of the simulation these particles “aged”, hence \( f_N \) increased.

Similar arguments apply to \( f_{\text{BC}} \). One hour after the simulation started, only 10% of the BC mass concentration was contained in the activated cloud droplets. This value increased quickly during the next 7 hours until \( f_{\text{BC}} \) was about 80% at \( t_p = 8 \text{ h} \). For cloud parcels from \( t_p = 40 \text{ h} \) onwards almost 100% of the BC mass concentration was incorporated in the cloud droplets. Note that the dependence of \( f_N \) and \( f_{\text{BC}} \) on plume time \( t_p \) is the result of the interplay of the numerators’ and denominators’ magnitudes, and that both the total
aerosol number concentration \( N_a \) and the total BC mass concentration display a very pronounced characteristic temporal profile shown in Figure 2.1b and d for reasons discussed in Section 2.4.2.

However, the aging process was not necessarily monotone. For the cloud parcels between \( t_p = 9 \) h and \( t_p = 12 \) h \( f_N \) and \( f_{BC} \) decreased before increasing again. This behavior was caused by the timing of the emissions and the production of condensable hygroscopic material. Emissions of diesel and gasoline particles were ongoing until \( t_p = 12 \) h (1800 LST). The particles emitted in the late afternoon did not age as quickly as the ones in the late morning, since photochemistry had slowed down by that time, hence the decrease in \( f_N \) and \( f_{BC} \). These quantities started increasing again after emissions had stopped. Further process analysis revealed that both condensation and coagulation contributed to the aging process in this urban plume scenario. However the relative importance of the two aging mechanisms depended on the time of the day. During the day condensation was the dominant aging process, since condensable secondary aerosol mass was readily produced by photochemistry. During the night these processes ceased and coagulation of BC-containing particles with large, hygroscopic background particles became more important (Riemer et al., 2010).

The left panel of Figure 2.9 shows the effective radius \( r_{eff} \) of the cloud droplet mode at \( t_c = 10 \) min as a function of \( t_p \). The effective radius is important for cloud radiative transfer and remote sensing calculations (Brenguier et al., 2000; Liu and Daum, 2002; Feingold et al., 2003; Feingold, 2003; Twohy et al., 2005) and defined as the ratio of the third moment to the second moment of the cloud droplet size number distribution:

\[
\begin{align*}
    r_{eff} &= \frac{\int_{r_{min}}^{\infty} r^3 n(r)dr}{\int_{r_{min}}^{\infty} r^2 n(r)dr},
\end{align*}
\]

where the \( r_{min} \) equals 1 \( \mu m \) and \( n(r) \) is the number size distribution in terms of wet radius, \( r \), of the particles. For the different cloud parcel simulations of the base case \( r_{eff} \) ranged between 5.5 \( \mu m \) and 8.5 \( \mu m \). The lowest values were obtained for the cloud parcels initialized with
Figure 2.9: (a) The same figure as Fig. 2.7, but for effective radius $r_{\text{eff}}$ at $t_c = 10$ min as a function of plume time $t_p$. (b) Relationship between the total cloud droplet number concentration $N_d$ and the effective radius $r_{\text{eff}}$.

aerosol populations around $t_p = 11$ h. These were the parcels with the highest aerosol number concentrations (cf. Figure 2.1) and also the highest cloud droplet number concentration, consistent with the first indirect effect (Twomey, 1974) given that the liquid water content is the same for each cloud parcel. The right panel of Figure 2.9 shows $r_{\text{eff}}$ versus the corresponding cloud droplet concentration $N_d$ and shows the relationship of $r_{\text{eff}} \sim N_d^{-1/3}$ for all the simulation scenarios presented. This relationship is expected for adiabatic conditions (McFarquhar and Heymsfield, 2001), but in reality the exponent can deviate significantly from 1/3 (McComiskey et al., 2009).

Figure 2.10 displays the relative spectral dispersion $\epsilon$ of the cloud droplet mode at $t_c = 10$ min as a function of $t_p$. The dispersion of the cloud droplet spectrum is of interest for cloud parameterization schemes related to warm rain processes and auto-conversion rates (Liu and Daum, 2000; Rotstaysn and Liu, 2003) and for parameterizing the effective radius of cloud droplets in global climate models (Liu and Daum, 2002; Peng et al., 2002).

The values range between 0.017 and 0.11, with the largest values occurring for the cloud parcels initialized with aerosol distributions around $t_p = 11$ h, coinciding with the cloud parcel with the smallest effective radius and largest cloud droplet number concentrations. This is consistent with Liu and Daum (2002) who conclude from field data that polluted clouds are associated with larger relative dispersion.
2.5.3 Impact of cooling rate on the reference case

In addition to the base case that used a cooling rate of 0.5 K/min, Figures 2.7–2.10 include the results of two additional simulations with a cooling rate of 0.25 K/min and 1 K/min, respectively. The results show expected behavior. A higher cooling rate lead to higher supersaturation values (Figure 2.7). While the base case values ranged between 0.2% and 0.34%, the cooling rate of 1 K/min resulted in a range of 0.28% and 0.49%, and the cooling rate of 0.25 K/min yielded a range of 0.16% to 0.25%. The qualitative dependence on plume time is the same for the three cooling rates with the lowest supersaturation values obtained during the plume times with the largest abundance of aerosol particles.

Figure 2.8 shows that a higher cooling rate generally lead to larger values of \( f_N \) and \( f_{BC} \). For example on the second day of simulation the cooling rate of 1 K/min yielded \( f_N \) of 80% whereas the cooling rate of 0.25 K/min plateaued at 58%. However, the differences in \( f_N \) and \( f_{BC} \) for at early plume hours are relatively small. This can be explained by the fact that these aerosol populations contained fresh emissions, which were not accessible for activation for the supersaturations produced by either of the three cooling rates. This can also be seen in Figure 2.4a, which shows that the maximum of the number concentration distribution \( n(D_{dry}, s_c) \) for the upper branch representing the fresh emissions lies mostly above a supersaturation of 1%.
Figure 2.9 shows that with a higher cooling rate a higher effective radius was reached. The range with respect to plume time was enhanced when the cooling rate was higher, between 6 µm and 10 µm for 1 K/min versus 5 µm and 7 µm for 0.25 K/min. The relative dispersion shows the opposite behavior, with the largest values attained for the lowest cooling rate as evident in Figure 2.10.

2.6 Quantifying the importance of mixing state

We will now turn to the question of how important it is to know the mixing state for understanding aerosol activation and the nucleation-scavenging of BC. To answer this question, we took the following approach: In addition to the reference case (scenario “ref”), where we used particle-resolved model results as input for the cloud parcel model, we performed three different averaging procedures on the particle-resolved data before using them as parcel model input. Specifically we distinguish between composition averaging (scenario “comp”), size-bin averaging (scenario “size”), and averaging of both composition and size (scenario “both”). All three averaging scenarios were implemented by binning the particle-resolved aerosol population (“ref”) into 20 logarithmically spaced size bins from 1 nm to 10 µm. The number of particles in each bin remained unchanged by the averaging procedures.

For the scenario “comp” we assigned the bin-averaged composition to all particles within one size bin. The particle sizes remained unchanged. For the scenario “size” we assigned the bin-averaged particle volume to all particles within each size bin while preserving their per-particle species ratios. For the scenario “both” we applied composition averaging first, and then size-bin averaging. The resulting size distribution corresponds to a traditional moving-center sectional method (Jacobson, 1997). The detailed description of each procedure and their properties is given in Appendix B.
Figure 2.11: Two-dimensional number concentration distribution $n(D_{\text{dry}}, w_{\text{BC,dry}})$, at $t_p = 15$ h for scenarios (a) “ref”, (b) “comp”, (c) “size”, and (d) “both”. The results of only one member of the ensemble are shown.
2.6.1 Averaged simulation results

The purpose of the composition- and the size-bin-averaging scenario is to separate out the importance of composition resolution versus size resolution. Figures 2.11, 2.12 and 2.13 show for one member of the ensemble how the various averaging scenarios impacted the two-dimensional particle number concentration distributions \( n(D_{\text{dry}}, w_{\text{BC,dry}}) \), \( n(D_{\text{dry}}, \kappa) \), and \( n(D_{\text{dry}}, s_c) \). In the “comp” scenario, the particles in one size bin retained their original sizes, but their compositions were averaged as shown in Figure 2.11b. The corresponding \( n(D_{\text{dry}}, \kappa) \) distribution (Figure 2.12b) does not have the spread in \( \kappa \)-dimension as the reference case does. Instead of covering a wide range of \( \kappa \) values between near-zero and 0.65 the particles are mapped to a mean value of kappa of about 0.4 for large parts of the size spectrum. Likewise, the corresponding \( n(D_{\text{dry}}, s_c) \) distribution does not have the spread in \( s_c \) direction as the reference case does.

Since the “size” scenario forced particles in one bin to have the same size while they can have different compositions, the two-dimensional distributions appear as a number of vertical lines (Figure 2.11c, Figure 2.12c and Figure 2.13c). In the “both” scenario, the size-bin averaging was done after composition averaging, thus all particles had the same sizes and compositions and the two-dimensional particle number distributions were reduced to one point per size bin, as shown in Figures 2.11d, 2.12d and 2.13d.

Using these modified initial conditions, we compared the maximum supersaturation \( s_{\text{max}} \) attained during the 10-min parcel time, the cloud droplet fraction \( f_N \), the nucleation-scavenged fraction \( f_{\text{BC}} \), the effective radius \( r_{\text{eff}} \), and the relative spectral dispersion \( \epsilon \). The four latter quantities are reported at \( t_c = 10 \text{ min} \). We used the reference case as a benchmark for comparison to the three averaging schemes. Any differences can be attributed to the differences in the representations of the size and composition of the aerosol particles. Figures 2.14–2.16 show the results for the base-case cooling rate of 0.5 K/min. We will summarize the impact of a different cooling rate value at the end of this section.
Figure 2.12: Two-dimensional number concentration distribution $n(D_{\text{dry}}, \kappa)$, at $t_p = 15$ h for scenarios (a) “ref”, (b) “comp”, (c) “size”, and (d) “both”. The results of only one member of the ensemble are shown.
Figure 2.13: Two-dimensional number concentration distribution $n(D_{\text{dry}}, s_c)$, at $t_p = 15$ h for scenarios (a) “ref”, (b) “comp”, (c) “size”, and (d) “both”. The results of only one member of the ensemble are shown.

Figure 2.14: Maximum supersaturation, $s_{\text{max}}$, attained in the 10-minute parcel simulations using the base-case cooling rate of 0.5 K/min as a function of plume time $t_p$ for the reference case and the averaging scenarios. The figure shows the average of an ensemble of 10 simulations.
Figure 2.14 compares the attained maximum supersaturation $s_{\text{max}}$ for the individual averaging scenarios to the reference case. The results are very close to each other, indicating that the impact of mixing state on the maximum saturation ratio is small under the conditions investigated here and that the number concentration of aerosol particles is the main driver for $s_{\text{max}}$. The largest (absolute) difference was $\Delta s_{\text{max}} = 0.017\%$ and occurred for scenario “both” at $t_p = 3\ h$. At that time the reference case shows a largely externally mixed particle population (similar to Figure 2.2a).

Figure 2.15 shows $f_N$, $f_{\text{BC}}$, $r_{\text{eff}}$ and $\epsilon$ as a function of $t_p$ for the four scenarios. We give the range of relative errors for all 48 cloud parcel simulations in Table 2.2. For the cloud droplet fraction $f_N$ shown in Figure 2.15a, composition averaging and size-bin averaging lead to relatively small errors ($-3\%$ to $25\%$ for scenario “comp” and $-2\%$ to $11\%$ for scenario “size”). Larger errors ($-10\%$ to $35\%$) arose for scenario “both”, where we averaged both size and composition. Since for this case the particles in one size bin were assigned the same size and composition, all the particles in that bin simultaneously either activated or did not activate. This caused the sudden jump in $f_N$ at $t_p = 35\ h$, and from further investigations we concluded that this behavior is sensitive to the imposed bin positions.

Figure 2.15b shows $f_{\text{BC}}$ as a function of $t_p$. The scenario “size” follows the reference case closely with differences ranging from $-15\%$ to $+5\%$. The “comp” and the “both” scenarios always overestimate $f_{\text{BC}}$, with overestimations up to $600\%$. Note that the stochastic variability of the model results indicated as error bars by the 95%-confidence interval is very small, so that the differences found here are indeed due to the different treatment of aerosol mixing state. For $t_p = 30\ h$ onwards the differences between the four scenarios become very small and $f_{\text{BC}}$ reaches $100\%$. The reasons for the relatively large errors seen for $f_{\text{BC}}$ in Figure 2.15b compared to the small errors for $f_N$ will be further discussed below.

Figures 2.15c and 2.15d show $r_{\text{eff}}$ and $\epsilon$ as a function of $t_p$. The “size” and “comp” scenarios result in values very close to the reference case. Scenario “both” results in larger differences, within $-9\%$ to $+4\%$ for $r_{\text{eff}}$ and from $-47\%$ to $+50\%$ for $\epsilon$. 
Activation fraction $f$

<table>
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<th>$\dot{T}$</th>
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<th>“size”</th>
<th>“both”</th>
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<tr>
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<td>$-3.0%$ to $+24%$</td>
<td>$-15%$ to $+17%$</td>
<td>$-38%$ to $+85%$</td>
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<td>$-3.1%$ to $+24%$</td>
<td>$-2.2%$ to $+11%$</td>
<td>$-10%$ to $+34%$</td>
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<td>$-2.4%$ to $+9.3%$</td>
<td>$-26%$ to $+65%$</td>
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</table>

BC scavenging fraction $f_{BC}$

<table>
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<th>“size”</th>
<th>“both”</th>
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<td>$-19%$ to $+6.7%$</td>
<td>$-0.37%$ to $+610%$</td>
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<td>$+0.0%$ to $+550%$</td>
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Effective radius $r_{eff}$

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<td>$-3.5%$ to $+0.50%$</td>
<td>$-8.8%$ to $+3.6%$</td>
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<td>$-2.7%$ to $+0.81%$</td>
<td>$-15%$ to $+10%$</td>
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Dispersion $\epsilon$

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<th>“size”</th>
<th>“both”</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-0.25$ K/min</td>
<td>$-9.3%$ to $+32%$</td>
<td>$-33%$ to $+120%$</td>
<td>$-73%$ to $+420%$</td>
</tr>
<tr>
<td>$-0.50$ K/min</td>
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<td>$-24%$ to $+19%$</td>
<td>$-47%$ to $+50%$</td>
</tr>
<tr>
<td>$-1.0$ K/min</td>
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<td>$-13%$ to $+36%$</td>
<td>$-59%$ to $+340%$</td>
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</table>

Table 2.2: Relative error ranges for four physical quantities ($f_N, f_{BC}, r_{eff}, \epsilon$) when computed from the three different averaging schemes (“comp”, “size”, “both”) and compared to the fully-particle-resolved results (“ref”). The relative error ranges are for one representative of the ten members in the ensemble and give the smallest and largest errors (negative values are under-predictions, positive values are over-predictions) observed from $t_p = 1$ h to $t_p = 48$ h (i.e., excluding the first hour of simulation). The minimum and maximum values of the error for any given physical quantity do not generally occur at the same plume time as each other, or as the counterparts for another physical quantity.
Figure 2.15: (a) Cloud droplet number fraction $f_N$, (b) nucleation-scavenged BC mass fraction, $f_{BC}$, (c) effective radius, $r_{eff}$, and (d) the relative spectral dispersion, $\epsilon$ for the reference case and averaging scenarios using the base-case cooling rate of 0.5 K/min. Each figure shows the average of an ensemble of 10 simulations.
The magnitude of the errors in $r_{\text{eff}}$ amount approximately to 1/3 of the errors in $f_N$ (Kristjansson, 2002). This can be shown by writing $r_{\text{eff}}$ as (Rotstayn and Liu, 2003):

$$r_{\text{eff}} = \left(1 + 2\epsilon^2\right)^{\frac{3}{2}} \left(\frac{3L}{4\pi \rho_w}\right) N_d^{-\frac{1}{4}},$$

(2.16)

where $L$ is the liquid water content. Given that $L$ is constant and that the value for $\epsilon$ is smaller than 0.1, error propagation yields an approximation for the relative error in $r_{\text{eff}}$:

$$\frac{|\Delta r_{\text{eff}}|}{r_{\text{eff}}} \lesssim 2\epsilon^2 \frac{|\Delta \epsilon|}{\epsilon} + \frac{1}{3} \frac{|\Delta N_d|}{N_d} \approx \frac{1}{3} \frac{|\Delta N_d|}{N_d},$$

(2.17)

where the final approximation is assuming that $|\Delta \epsilon|/\epsilon$ is of a similar magnitude as $|\Delta N_d|/N_d$.

The order of magnitude of errors in cloud optical properties as a result of errors in $r_{\text{eff}}$ can be estimated as follows: The maximum error for $r_{\text{eff}}$ occurs for scenario “both” at $t_p = 12$ h and represents an underprediction of $r_{\text{eff}}$ of about 10%. Assuming constant cloud thickness and cloud liquid water content, the optical depth $\tau$ is inversely proportional to the effective radius, and this underprediction in $r_{\text{eff}}$ would thus lead to an increase in optical depths by 10%. The cloud albedo $\alpha$ is given to a good approximation by Meador and Weaver (1980) as

$$\alpha = \frac{(1 - g)\tau}{1 + (1 - g)\tau},$$

(2.18)

where $g$ is the asymmetry parameter. For the scattering of solar radiation by clouds $g \approx 0.85$. If the original optical depth is 15, a relative error of 10% in $r_{\text{eff}}$ translates to an increase in the cloud albedo by 2%. For an optical depth of 10, the corresponding increase in cloud albedo would be 2.3%.

Compared to $r_{\text{eff}}$, the errors in $\epsilon$ are comparatively large. Considering that $\epsilon$ is the ratio of standard deviation to mean diameter, we found that the large error is introduced by errors in the standard deviation (not the mean diameter).

In summary, the scenario “both” showed the largest deviations from the reference case.
for all four quantities, \( f_N, f_{BC}, r_{\text{eff}} \) and \( \epsilon \). This is not surprising, since this averaging scenario corresponds to the largest manipulation of the reference aerosol population. Interestingly, even for large plume times \( t_p \), which are usually identified with a high degree of “aging”, the error in scenario “both” did not necessarily vanish, as Figure 2.15a shows. Also, while size-bin averaging consistently resulted in small errors, the magnitude of the error due to composition averaging was larger for \( f_{BC} \) than for \( f_N \).

To elucidate the latter we analyzed the cloud droplet population as shown in Figure 2.16. The solid line in Figure 2.16a shows \( f_N \) for the reference case. The other lines show \( f_N \) segregated according to the dry BC mass fraction \( w_{BC,\text{dry}} \) of the CCN that formed the cloud droplets. The largest contribution (thin solid line) came from aerosol particles with \( w_{BC,\text{dry}} \) between 0% and 20%. These particles contributed on average 88% of the CDNC during the two days. Aerosol particles with \( w_{BC,\text{dry}} \) between 20% and 40% (thin dashed line) contributed on average about 10% of the CDNC, and only about 2% of the CDNC were attributed to particles with \( w_{BC,\text{dry}} \) larger than 40% (thick dashed line). Figures 2.16b–d show that while \( f_N \) was replicated well for each averaging scenario, only the size-bin-averaging scenario also replicated the information on mixing state well (Figure 2.16c). Due to the composition averaging in scenarios “comp” and “both”, the mixing state information was distorted. In particular, these cases had very few particles with higher \( w_{BC} \) compared to the reference case, as evident in Figure 2.11, leading to the observed differences in \( f_{BC} \).

### 2.6.2 Impact of cooling rate on the averaged simulation results

We repeated the sets of averaged simulations for the two different cooling rates (0.25 K/min and 1 K/min). The finding shown in Figure 2.14 for the cooling rate of 0.5 K/min holds for the other cooling rates as well, namely that \( s_{\text{max}} \) is not impacted by the different averaging scenarios. Table 2.2 gives a summary of the range of errors for the four different physical quantities. Several studies found a larger sensitivity of CCN properties to the underlying aerosol for small cooling rates (low updraft velocities) (e.g. Ervens et al. (2010)). For our
Figure 2.16: Cloud droplet number fraction $f_N$ segregated according to the BC dry mass fraction $w_{BC,\text{dry}}$ of the underlying aerosol population. (a) the scenario “ref”, (b) scenario “comp”, (c) scenario “size” and (d) scenario “both”. The thick solid line represents the total cloud droplet number fraction. The thin solid, thin dashed and thick dashed lines depict the cloud droplet number fraction with $0\% < w_{BC,\text{dry}} \leq 20\%$, $20\% < w_{BC,\text{dry}} \leq 40\%$, and $w_{BC,\text{dry}} > 40\%$, respectively.
results this applies for some quantities and averaging scenarios, but not for all. A clear dependence on cooling rate for all averaging scenarios was seen for $f_{BC}$ with the largest errors occurring at the lowest cooling rate ($-7.2\%$ to $840\%$ for scenario "both" and the cooling rate of $0.25$ K/min). For $f_N$, $\epsilon$ and $r_{\text{eff}}$ there is not such a clear trend evident.

### 2.6.3 Connections to other studies

Several prior studies on CCN activation have explored certain aspects of the importance of mixing state. For example, *Kuwata and Kondo* (2008) reported evidence for the occurrence of a particle population with non-uniform mixing states in the urban atmosphere of Tokyo. They pointed out the importance of BC-containing particles in controlling CCN concentrations in an urban environment with fresh emissions and concluded that particles with large non-volatile cores (presumably consisting of BC) were largely CCN-inactive. This is in agreement with our findings showing that particles with large BC content ($w_{BC,\text{dry}} > 40\%$) contribute very little to the CCN concentration, which leads to low values of $f_N$ during early plume hours.

*Medina et al.* (2007) investigated CCN closure for aerosols representing polluted continental conditions from the Great Lakes area during ICARTT 2004. They found that assuming size-dependent composition lead to improved closure but that overprediction still occurred in some instances. Size-dependent composition corresponds to our scenario “both”, and we also see an overprediction for $f_N$ for most plume hours since the detailed composition information is lost.

*Wang et al.* (2010) investigated CCN properties for Mexico City. They concluded that the CCN concentration can be derived within $20\%$ assuming internal mixture if a great majority of particles have overall $\kappa > 0.1$ and that the increase of $\kappa$ to such a value occurs within a few hours during daytime. Our results are broadly consistent with their findings, however we would like to point out that in a polluted environment where emissions age quickly, fresh emissions are likely to be replenished continuously, which can lead to an overestimation of
CCN and CDNC concentrations when an internal mixture is assumed.

*Anttila* (2010) performed cloud parcel modeling studies using a sectional model approach with input particle populations based on observational data, including both size and hygroscopicity information. The author showed that assuming an internal mixture for externally mixed urban and rural particle populations lead to errors in CDNC up to 35%, compared to 12% for marine and continental background. While this work is similar in spirit to our study, we have used a reference particle population that fully resolves the complex mixing state of the aerosol, without a priori assumptions. The errors we observed due to averaging are of a similar magnitude to those found by *Anttila* (2010).

An important distinction between studies on CCN closure and our study is that we do not use predefined supersaturation thresholds but rather we include the competition for water vapor. The buffering impact of this is most evident for the early plume hours, when fresh emissions coexist with hygroscopic background particles in separate subpopulations. The averaged simulations lead to some overestimation of $f_N$, however the error is not as large as one might expect, since the resulting supersaturation is also impacted and in this case it is somewhat lower than in the reference case. These findings are consistent with the results reported in *Cubison et al.* (2008) and *Ervens et al.* (2010), who pointed out that differences in model results and observations were reduced when allowing for feedback of the particles on supersaturation. Further, *Ervens et al.* (2010) concluded that initially hydrophobic particles are sufficiently processed within a few kilometers downwind and that an internal-mixture assumption may be appropriate to obtain closure. However, they added the caveat that this simplified composition may not necessarily represent actual properties. This is confirmed by our findings on the predictions of $f_N$ versus $f_{BC}$. While the error in $f_N$ was relatively small (within 35% for the base-case cooling rate) for all averaging scenarios, this agreement was obtained for the wrong reasons. This became evident when we predicted another quantity ($f_{BC}$), for which the error then was much larger.
2.7 Size-resolved nucleation-scavenging fraction of black carbon-containing aerosol

When BC aerosols serve as CCN and are incorporated into cloud droplets, they can be removed from the atmosphere if the cloud precipitates. This determines the abundance of BC particles, their lifetime in the atmosphere, and hence their impact on climate. For a more thorough understanding of direct, semi-direct and indirect effects of BC in the atmosphere, it is important to investigate the nucleation-scavenging fraction of BC aerosol.

During the Whistler Aerosol and Clouds Study 2010 (WACS-2010) campaign measurements of BC mass in individual cloud droplets were performed using a single particle soot photometer (SP2), an ultra-high sensitivity aerosol spectrometer (UHSAS) and a scanning mobility particle sizer (SMPS) at the Whistler high elevation site in British Columbia (Schroder et al., 2011). The measurements are available for a size range of 89-229 nm for the cloud droplet residuals. Schroder et al. (2011) demonstrated that for the conditions during the campaign the BC nucleation-scavenging fractions ranged between 13% and 23%. Further, no significant size dependence of the black carbon scavenging fraction was found. An example of one case is shown in Figure 2.17. While a rigorous comparison of these observations to our model results is not possible because many of the inputs to constrain the model simulations are unknown, it is nevertheless still instructive to conduct a qualitative comparison.

Using the output from our cloud parcel simulations the BC scavenging fraction as a function of dry diameter is calculated and shown in Figure 2.18. The four panels illustrate the results of the simulations initialized by aerosol populations at $t_p=1\,\text{h}$, $t_p=7\,\text{h}$, $t_p=15\,\text{h}$ and $t_p=36\,\text{h}$.

In contrast to the observations, there is an evident size dependence of the simulated BC nucleation scavenging fractions. Comparing the scavenging fraction at various plume times, for example at the cooling rate of 1 K/min, the fraction reaches 50% at different sizes,
Figure 2.17: Size-resolved nucleation-scavenging fraction of black carbon-containing aerosol measurement by Schroder et al. (2011) during WACS-2010 campaign. Figure adapted from Schroder et al. (2011).

Figure 2.18: Size-resolved nucleation-scavenging fraction of black carbon-containing aerosol at four selected plume time, $t_p=1$ h (top left), $t_p=7$ h (top right), $t_p=15$ h (bottom left) and $t_p=36$ h (bottom right). Blue, green and red lines indicate the cooling rate of 1 K/min, 0.5 K/min and 0.25 K/min respectively.
2.2 \times 10^{-1} \mu m, 7.7 \times 10^{-2} \mu m, 8.9 \times 10^{-2} \mu m and 4.8 \times 10^{-2} \mu m respectively at \( t_p = 1 \) h, \( t_p = 7 \) h, \( t_p = 15 \) h and \( t_p = 36 \) h. The difference in the size dependence of BC nucleation scavenging is determined by the differences in size distributions of BC mass concentration in both cloud droplet population and total particle population. As the BC particles become more internally mixed with other aerosol species at later plume times as shown in Figure 2.2, particles of smaller size are susceptible to nucleation scavenging, however, the amount and fraction of scavenging is constrained by amount of BC contained in the underlying aerosol population as well.

The scavenging fraction is higher for larger cooling rate for the aerosol particles having the same dry diameter. For example, at \( t_p = 7 \) h, for particles of \( 10^{-1} \mu m \) in dry diameter, the scavenging fraction is 84\%, 59\%, and 18\% for 1 K/min, 0.5 K/min and 0.25 K/min, respectively. While this is expected, it is interesting to note that the sensitivity to cooling rate is smallest at \( t_p = 1 \) h (Figure 2.18 top left panel) for size between \( 1 \times 10^{-1} \mu m \) and \( 2 \times 10^{-1} \mu m \) and the fraction is significantly smaller compared to the counterparts at the other three plume times. This is consistent with Figure 2.4, which shows that at \( t_p = 1 \) h most of the BC particles being freshly emitted have still rather high critical supersaturations. The three cooling rates used here do not produce high enough supersaturations to activate many of these particles, hence the sensitivity to cooling rate is limited.

Although no quantitative comparison between the field observations and the model output is possible, a qualitatively comparison of the results shown in Figure 2.18 and that from the Whistler Aerosol and Clouds Study (WACS-2010) in 2010 (Schroder et al., 2011) reveals differences in the size dependence of the BC nucleation scavenging fraction.

This discrepancy may be due to underlying differences in the aerosol populations present during the field campaign and in the model input. The overall low BC scavenging fractions in the observations may indicate that the BC particles were either uncoated or coated with rather hydrophobic aerosol species such as secondary organic aerosol. Besides, instrument errors and atmospheric conditions like entrainment or turbulence may contribute to the
disparity between the two sets of results.

In summary, from this analysis we conclude that observations like the ones made by Schroder et al. (2011) here are suitable and interesting to compare to the model output. However, to make a comparison of field observations and model simulations quantitative, detailed measurements of the model inputs are necessary, including the characterization of the below-cloud aerosol populations and the updraft velocity.

2.8 Analysis of kinetic limitation of cloud droplet growth

2.8.1 Introduction

It has been suggested that cloud droplet growth may be limited kinetically, causing the cloud droplet number concentration actually achieved to be lower that what is predicted by equilibrium Köhler theory (Nenes et al., 2001; Chuang et al., 1997). The overestimation of cloud droplet number concentration can lead to subsequent error in cloud radiative effect calculation. Nenes et al. (2001) pointed out that the kinetic limitation is important when considering effects of clouds for regional climate. The objective of this section is to demonstrate the capability of particle-resolved model framework developed in this dissertation in the identifying different types of the kinetic limitation mechanisms.

According to equilibrium Köhler theory, the cloud condensation nuclei (CCN) with critical supersaturations less than the maximum environmental supersaturation attained during a cloud parcel ascent are assumed to form cloud droplets. The validity of this assumption hinges on whether droplets reach equilibrium with the environment instantaneously.

However, it is not necessarily the case that the particles reach equilibrium with the environment instantaneously. Further, it takes a certain amount of time for the CCN to reach their critical diameters. Depending on the amount of the time for the CCN to reach
their critical diameters, and the evolution of the environmental water vapor saturation ratio, kinetic limitation can be classified into three types as suggested by Nenes et al. (2001). The three types of the kinetic limitation mechanisms are briefly introduced as follows.

First, if the time a particle needs to attain the critical diameter is longer than the duration under which the environmental saturation ratio exceeds the equilibrium saturation of the particles, although the maximum environmental saturation is larger than the critical supersaturation, the particle will not form cloud droplets. This type of limitation is called the “evaporation mechanism”.

Second, after the cloud parcel environment attains the maximum saturation ratio, the environmental saturation ratio starts to decrease. If the environment saturation ratio decreases to an extent that it drops below the equilibrium saturation ratio of the activated droplet, then the cloud droplet will evaporate. This is called the “deactivation mechanism”.

The third type of kinetic limitation occurs for those particles with very low critical supersaturations relative to the environmental saturation ratio because of their large sizes. These particles grow continuously since the environmental saturation ratio is always larger than their equilibrium saturation ratios, however they may never form cloud droplets because of their critical diameters are so large that they take an exceedingly long time to grow to those sizes. This type of limitation is called the “inertial mechanism”.

To identify the different types of kinetic limitation, we need to analyze the history of the cloud parcel saturation ratios and the histories of equilibrium saturation ratio of individual particles. We will carry out this analysis for some of the cloud parcel simulations presented earlier in this chapter.

2.8.2 Methodology

In this section, the aerosol populations at \( t_p = 1 \) h, 12 h, 24 h and 48 h from are used to initialize cloud parcel model simulations using three different cooling rates of 0.15 K min\(^{-1}\), 0.5 K min\(^{-1}\) and 0.85 K min\(^{-1}\), yielding a total of 12 model simulations. To identify the
### Status of the particle Criteria

<table>
<thead>
<tr>
<th>Status of the particle</th>
<th>Criteria</th>
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<tbody>
<tr>
<td>Activated</td>
<td>$D_{\text{wet}} &gt; D_{\text{crit}}$ for $[t_0 &lt; 600 \text{ s}, t_1 = 600 \text{ s}]$</td>
</tr>
<tr>
<td>Deactivated</td>
<td>$D_{\text{wet}} &gt; D_{\text{crit}}$ for $[0 \text{ s} &lt; t_0 &lt; 600 \text{ s}]$ and $D_{\text{wet}} &lt; D_{\text{crit}}$ at $[t_1 = 600 \text{ s}]$</td>
</tr>
<tr>
<td>Inertial</td>
<td>$(D_{\text{wet}} &lt; D_{\text{crit}}$ and $S_{\text{eq}} &lt; S_{\text{env}}$) for $[(0 \text{ s} &lt; t_0 &lt; 600 \text{ s})$ and $t_1 = 600 \text{ s}]$</td>
</tr>
<tr>
<td>Interstitial</td>
<td>$(D_{\text{wet}} &lt; D_{\text{crit}}$ and $S_{\text{eq}} \geq S_{\text{env}}$) for $[(0 \text{ s} &lt; t_0 &lt; 600 \text{ s})$ and $t_1 = 600 \text{ s}]$ and $S_{\text{crit}} \geq S_{\text{max}}$</td>
</tr>
<tr>
<td>Evaporated</td>
<td>$(D_{\text{wet}} &lt; D_{\text{crit}}$ and $S_{\text{eq}} \geq S_{\text{env}}$) for $[(0 \text{ s} &lt; t_0 &lt; 600 \text{ s})$ and $t_1 = 600 \text{ s}]$ and $S_{\text{crit}} &lt; S_{\text{max}}$</td>
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Table 2.3: Criteria of various kinetic limitation mechanism. $D_{\text{crit}}$ and $D_{\text{wet}}$ are the critical diameter and wet diameter of the particle. $S_{\text{eq}}$ and $S_{\text{crit}}$ are equilibrium saturation and critical supersaturation of the particle. $S_{\text{env}}$ is the environmental saturation, and its maximum is denoted by $S_{\text{max}}$.

First we compare the cloud droplet number concentration obtained from equilibrium to the one from particle-resolved simulation. From Figure 2.19, the prediction of droplet number concentration based on equilibrium Kohler theory leads to an overestimation of the cloud droplet number concentration for the 12 simulations, however the extent depends on the conditions. The cloud droplet number concentration $N_d$ obtained from parcel simulations ranges between 50% and 90% of their counterparts obtained assuming equilibrium Kohler theory. This is similar to the amount of overestimation suggested by Nenes et al. (2001).

**2.8.3 Results**

First we compare the cloud droplet number concentration obtained from equilibrium to the one from particle-resolved simulation. From Figure 2.19, the prediction of droplet number concentration based on equilibrium Kohler theory leads to an overestimation of the cloud droplet number concentration for the 12 simulations, however the extent depends on the conditions. The cloud droplet number concentration $N_d$ obtained from parcel simulations ranges between 50% and 90% of their counterparts obtained assuming equilibrium Kohler theory. This is similar to the amount of overestimation suggested by Nenes et al. (2001).
Figure 2.19: Cloud droplet number concentration, $N_d$, obtained from cloud parcel simulation versus $N_d$ computed assuming equilibrium theory. The cloud parcel simulations are initialized with particle-resolved aerosol populations at selected four plume times, $t_p=1$ h, 12 h, 24 h and 48 h. Blue, green and red indicate respectively the three cooling rates, 0.85 K min$^{-1}$, 0.5 K min$^{-1}$ and 0.15 K min$^{-1}$, under which the cloud parcel simulations are performed. Results from a total of 12 cloud parcel simulations are presented here.

In Figure 2.19, the cases where kinetic limitation is significant are those scenarios with high aerosol number concentrations. This is in agreement with Nenes et al. (2001), who stated that aerosol number concentration is a critical factor controlling kinetic effects.

By applying the criteria in Table 2.3 to the particle-level information regarding the parcel time $t_c$ history of the equilibrium saturation ratios, critical diameters and wet diameters of individual particles and environmental relative humidity, the effect on cloud droplet formation due to kinetic limitation is attributed to various types of mechanisms. Almost all the limitations are attributed to the deactivation mechanism for the urban plume scenarios presented.
2.9 Conclusion

In this study we described the use of the particle-resolved aerosol model PartMC-MOSAIC in conjunction with a cloud parcel model to quantify the importance of mixing state information for cloud droplet activation. We simulated an idealized urban plume scenario tracking the composition of about 10,000 computational particles over the course of 48 hours. We then used the simulated particle populations at each of the 49 hours as input for a 10-minute cloud parcel simulation. These simulated activation and condensational growth of the particle population as the parcel underwent cooling at a prescribed rate and the individual particles competed for water vapor. We used the SUNDIALS implicit BDF solver for the integration of the ODE system describing the cloud parcel.

The maximum supersaturation reached in the individual cloud parcel simulations for the base case of 0.5 K/min ranged between 0.20% and 0.35%. This difference was exclusively caused by differences in the initial aerosol population. The fraction of particles that became cloud droplets generally increased when we initialized the cloud parcel model with particles from the later part of the 48-hour urban plume simulation. While during the morning of the first day the cloud droplet fraction amounted to 20%, this increased to about 70% by the end of the second day. This is consistent with the notion that the aerosol population during the early plume hours contained a large proportion of “fresh” soot particles, which were not easily activated. As a response higher maximum saturation ratios were reached. Over the course of the simulation these particles “aged”, hence the cloud droplet fraction increased. The same applied to the BC mass fraction that is nucleation-scavenged.

We then investigated the importance of size information versus composition information for the prediction of cloud droplet number concentration and nucleation-scavenged black carbon mass. From this the following picture emerged for the base-case cooling rate of 0.5 K/min: for the cloud droplet number fraction $f_N$, both composition averaging and size-bin averaging led to relatively small errors (less than 25% for all 48 cloud parcel simulations).
Larger errors (up to 34%) arose for the scenario where we averaged both size and composition. In contrast, for the nucleation-scavenged black-carbon mass $f_{BC}$ the results for size-bin averaging tracked the reference case well, while composition averaging with or without size-bin averaging led to errors of up to 600%. Larger cooling rates lead to smaller errors for all averaging scenarios in $f_{BC}$, however for $f_N$, $\epsilon$ and $r_{eff}$ no such clear dependence emerged.

These results show that for the conditions simulated here, to accurately simulate black-carbon mass scavenging it is important to resolve the composition distribution within each size bin if fresh emissions coexist with hygroscopic aged emissions or other hygroscopic types of particles, although we have not quantified how much composition resolution is required. It is less important to resolve the particle composition for determining cloud droplet number fractions. We caution that our study does not take into account the effects of composition and size-bin averaging on the evolution of the urban plume simulation itself, as we used the fully resolved particle population in that case. It is likely that all types of averaging would introduce error in the urban plume evolution, which would then contribute to additional error in the predicted cloud droplet number fraction and nucleation-scavenged black-carbon mass. We note that our results are consistent with those of Dusek et al. (2006b), which are often stated as “size matters more than composition”, as we have considered altering the resolution of size information but we always modeled the size dependence of the aerosol distribution.

There have been a number of modeling and observational studies the importance of mixing state for CCN activation, including Cubison et al. (2008); Medina et al. (2007); Wang et al. (2010); Ervens et al. (2010); Kuwata and Kondo (2008); Dusek et al. (2006b); Anttila (2010). Common conclusions from these studies are that aerosol populations dominated by fresh emissions need size-resolved composition representation, whereas size-resolved composition is less important for “aged” particles, and that differences in CCN decrease if CDNC are considered. All of these findings are consistent with our study as detailed in Section 2.6.3. However, we go beyond this as we consider the fact that true aerosol populations have not
merely size-dependent composition, but a significant range of compositions at each size. Our results show that adequately predicting CCN number does not generally result in accurate prediction of other quantities, such as scavenged BC fraction. This is reasonable as fitting the CCN spectrum is merely a one-dimensional constraint on a complex multi-dimensional aerosol population.
Chapter 3

Sensitivity of aerosol mixing state impacts on cloud microphysical quantities to environmental conditions

Chapter 2 (published in Ching et al. (2012)) presented the fundamentals of this thesis, i.e. the model description of the particle-resolved cloud parcel model and the framework for quantifying the importance of BC mixing state for cloud microphysical quantities. However, the findings shown in Chapter 2 only relied on one urban plume scenario. In Chapter 3 we systematically explore a wider range of environmental conditions to generalize the conclusions made in Chapter 2. Further, this chapter describes a process-level analysis to attribute changes in cloud droplet number concentrations between different scenarios to changes in the underlying aerosol populations compared to changes in the response of the maximum saturation ratio in the cloud parcel. This chapter is prepared as a journal article for submission to the Journal of Geophysical Research.

3.1 Introduction

Black-carbon-containing particles originate from fossil fuel combustion, as well as from biomass and biofuel burning (Cooke and Wilson, 1996; Bond et al., 2004). They absorb solar radiation, which causes a warming of the atmosphere where these particles reside (Jacobson, 2001; Seinfeld, 2008; Ramanathan and Carmichael, 2008; Feichter and Stier, 2012).
Because of this warming effect, black carbon emission reductions have been suggested as a short-to-medium-term mitigation strategy to combat global warming, alongside with greenhouse gas emission control policies (Jacobson, 2002).

On the other hand, black-carbon-containing particles can act as cloud condensation nuclei (Hitzenberger et al., 1999; Dusek et al., 2006a; Andreae and Rosenfeld, 2008) and can therefore contribute to the aerosol indirect effect, which implies a cooling impact on climate (Koch et al., 2011). The competition of these two opposing climate impacts of black-carbon-containing particles makes it difficult to estimate the overall impact of black carbon (BC) mitigation strategies, and this problem has been recently elucidated in several modeling studies. For example, Chen et al. (2010) performed global model simulations to address this question and concluded that the decrease in the cloud droplet number concentration due to BC mitigation may weaken the aerosol indirect effect and hence the associated cooling of the climate. The changes in radiative forcing were +0.13 W m$^{-2}$ for 50% reduction of black carbon and organic carbon from fossil fuel alone, and +0.31 W m$^{-2}$ for 50% reduction in all primary sources of black carbon and organic carbon. Bahadur et al. (2012) studied the effects of BC mitigation on cloud properties for the region of California using parcel model simulations and global climate model simulations constrained by observations. Reducing BC emissions by 50% led to a reduction of 6% to 9% in cloud droplet number concentration. The reduction in droplet number concentration was associated with increased droplet size and decreased cloud albedo. Jacobson (2010) examined the impact of controlling emission of fossil-fuel BC particles on global temperature, precipitation and cloudiness and found that removing BC particles from fossil fuel combustion led to an average decrease of 0.3–0.5 K in surface temperature over a 15-year period. In contrast to Chen et al. (2010) and Bahadur et al. (2012), Jacobson (2010) found an increase of about 1% in cloud droplet number concentration after eliminating fossil fuel emission. Such increase was due to dynamic feedbacks such as the semi-direct effect that were accounted for in Jacobson (2010).

Whether a black-carbon-containing particle forms a cloud droplet hinges on its critical
supersaturation and the ambient saturation ratio. The critical supersaturation depends on the size and hygroscopicity of the black-carbon-containing particle, which are in turn determined by the aging processes that the particle is exposed to in the atmosphere (Furutani et al., 2008; Riemer et al., 2010). The environmental saturation ratio is determined by the characteristics of the entire aerosol population as well as the environmental updraft speed (Feingold et al., 2003; Reutter et al., 2009; Lu et al., 2012). The distribution of the per-particle composition within an aerosol population, i.e. the aerosol mixing state, can be complex (Moteki et al., 2007; Moffet and Prather, 2009; McMeeking et al., 2011; Cahill et al., 2012). It is challenging to represent the mixing state in aerosol models, because it requires tracking the multidimensionality of the aerosol population, with each aerosol species adding one dimension. For distribution-based models such as modal and sectional models, this becomes quickly computationally prohibitive, since the computational burden scales exponentially with the number of dimensions (i.e. chemical species). Hence, these models make simplifying assumptions regarding mixing state, but it is not clear what the error is that is introduced by this practice.

In contrast, stochastic particle-based methods scale with the number of particles and represent an appropriate tool for modeling aerosol particles when the per-particle composition is of interest. The recently developed model PartMC-MOSAIC (Riemer et al., 2009; Zaveri et al., 2008) is based on such an approach and explicitly simulates the composition of individual aerosol particles within a well-mixed Lagrangian air parcel without any a priory assumptions about mixing state.

In Ching et al. (2012) we used PartMC-MOSAIC for cloud parcel simulations and developed a method to quantify the errors in the activation of black-carbon-containing particles introduced by simplified aerosol mixing state representations. For a polluted urban plume scenario, neglecting differences in particle composition resulted in errors of less than 25% for the predictions of cloud droplet number fraction, while errors for the predictions in the nucleation-scavenged BC mass fraction amounted to up to 600%. Generally, relatively
small errors in cloud droplet number fraction did not necessarily translate to small errors in nucleation-scavenged BC mass fraction, however, these findings were based on only one particular urban plume scenario.

In this study, we investigate a wider range of environmental conditions to generalize the conclusions in Ching et al. (2012). Specifically, we probe the parameter space by varying four parameters, namely the BC emission rate, the background particle number concentration, the gas emission rate, and the cloud parcel cooling rate. The first three parameters influence how the aerosol particles age in the urban plume through coagulation, and condensation of secondary aerosol species. This consequently affects the hygroscopicity and critical supersaturation distribution of the particle population. Together with the fourth parameter (cooling rate) this determines the maximum saturation ratio attained in the cloud parcel, which critically affects the cloud droplet number concentrations (Feingold et al., 2003; Reutter et al., 2009).

The main contributions of this study are (1) developing a metric to attribute the differences in cloud droplet number concentration between any two environmental scenarios to differences in the underlying aerosol population characteristics compared to differences in the response of maximum saturation ratio attained in the cloud parcel, and (2) quantifying the sensitivity of the errors in calculating cloud microphysical properties due to simplified aerosol mixing state representation to a wide range of environmental conditions.

The chapter is structured as follows. Section 3.2 introduces the model framework. Section 3.3 describes the simulation setup. The results are then discussed in four separate sections. Section 3.4 presents the aerosol population characteristic of the suite of urban plume scenarios. It also discusses the results from the cloud parcel simulations, focusing on the cloud droplet number concentration and the aerosol activation fraction. In Section 3.5, we further show how to attribute changes in cloud droplet number concentrations to changes in the initial aerosol population versus the cloud parcel response. Section 3.6 gives the error quantification in activation fraction, the associated nucleation-scavenged fraction of black
carbon, the effective radius, and the relative spectral dispersion of cloud droplet spectrum due to simplified model representation in aerosol mixing states. In addition, section 3.6 compares the error in effective radius due to simplified mixing state representation to that in the effective radius parameterization. The impact of the error in effective radius on shortwave cloud albedo is also discussed in the same section. Conclusions are given in section 3.7.

3.2 Model Description

3.2.1 Particle-resolved Aerosol Model PartMC-MOSAIC

PartMC-MOSAIC (Particle Monte Carlo-Model for Simulating Aerosol Interactions and Chemistry) (Riemer et al., 2009; Zaveri et al., 2008) is a stochastic, particle-resolved model that simulates the evolution of the per-particle composition of a large number of aerosol particles within a well-mixed computational volume. The particle positions in the computational volume are not tracked. The full model description of PartMC-MOSAIC is given in Riemer et al. (2009). In brief, PartMC handles particle emission, particle dilution with background air, as well as Brownian coagulation among particles stochastically (Riemer et al., 2009). In this paper we used weighted particles in the sense of DeVille et al. (2011) to increase computational efficiency.

To allow for the treatment of aerosol chemistry, PartMC is coupled to the aerosol chemistry module MOSAIC (Zaveri et al., 2008). This includes the gas phase photochemical mechanism CBM-Z (Zaveri and Peters, 1999), a method for estimating activity coefficients of electrolytes and ions in aqueous solutions (Zaveri et al., 2005a), a solver for intraparticle solid-liquid partitioning (Zaveri et al., 2005b), and a solver for dynamic gas-particle partitioning (Zaveri et al., 2008). Secondary organic aerosol (SOA) is treated with the SORGAM (Secondary Organic Aerosol Model) (Schell et al., 2001). MOSAIC includes 77 gaseous species and 19 aerosol species. The latter are SO\(_4\), NO\(_3\), Cl, CO\(_3\), MSA (methanesulfonic acid), NH\(_4\), Na, Ca, other inorganic mass (which includes species such as SiO\(_2\), metal oxides,
and other unmeasured or unknown inorganic species present in aerosols), black carbon (BC),
and primary organic aerosol (POA). To represent SOA we use four model species originat-
ing from the oxidation of anthropogenic VOC precursors, and four model species from the
oxidation of biogenic VOC precursors. The model version of PartMC used here is version
2.2.0.

3.2.2 Particle-resolved Cloud Parcel Model

The details of the particle-resolved cloud parcel capability was described in Ching et al.
(2012). In brief, the cloud parcel model simulates the competition for water vapor among
aerosol particles that experience cooling at a prescribed cooling rate. For an input aerosol
population containing \(N_p\) particles, the system of ordinary differential equations consists of
\(N_p + 1\) equations, with one equation for the rate of change of the environmental saturation
ratio, \(S_v\), and \(N_p\) equations for the rate of change of wet diameter of each particle. For
numerical details of the cloud parcel model implementation, the readers are referred to
Appendix 1 in Ching et al. (2012). We do not consider any entrainment and collision-
coalescence among cloud droplets.

In Ching et al. (2012) we prescribed the cooling rate, but assumed constant pressure. Here
we updated the model to allow for pressure changes consistent with adiabatic conditions. To
simplify the numerical implementation we precalculated the pressure along the trajectory as
follows. During the subsaturated stage, the relationship between temperature and pressure
is dry adiabatic. Once saturation is reached, we use pseudo-moist adiabatic conditions to
describe the relationship between the temperature and pressure in the cloud parcel. The
rate of change of parcel pressure, \(dp/dt\), can be calculated from the constant cooling rate,
\(dT/dt\) as follows (Pruppacher and Klett, 1978),

\[
\frac{dp}{dt} = \frac{(c_{pa} + w_v c_{pc})p}{(R_a + w_v R_v)T} \frac{dT}{dt} + \frac{l_v p}{(R_a + w_v R_v)T} \frac{dw_v}{dt},
\]  

(3.1)
where \( w_v \) is water vapor mixing ratio, \( c_{pa} \) is the specific heat capacity of dry air, \( c_{pv} \) is the specific heat capacity of water vapor, \( R_a \) is the specific gas constant for dry air and \( R_v \) is the specific gas constant for water vapor. We calculate \( dw_v/dt \) using the Clausius-Clapeyron equation and the rate of change of temperature, \( dT/dt \) assuming all water vapor condenses in the saturated environment. From \( dp/dt \), together with the initial parcel pressure, a parcel-pressure time series can be precalculated and used as cloud parcel model input.

### 3.3 Description of Simulations

#### 3.3.1 Plume Time versus Parcel Time

Following the same strategy as in Ching et al. (2012), the simulations in this study were carried out as a two-stage process, the urban plume stage and the cloud parcel stage. For the urban plume stage, the evolution of an urban plume aerosol population in a sub-saturated environment was simulated using PartMC-MOSAIC. This was done in a Lagrangian approach, assuming that the parcel moved over a polluted urban environment for 48 h, starting at 6am local time. We refer to the time variable during the urban plume stage as *plume time* \( t_p \). An overview of the urban plume simulations is provided in Section 3.4.1. We focus our discussion on the particle populations at \( t_p = 1 \) h, 12 h, 24 h, and 48 h as they represent very different stages regarding the aging of BC-containing particles. At \( t_p = 1 \) h (7am local time), the population contained mainly freshly emitted BC-containing particles, while the population at \( t_p = 12 \) h (6pm local time) combined both freshly emitted particles as well as particles that were aged to various degrees. Particle and gas phase emissions were discontinued at \( t_p = 12 \) h, hence \( t_p = 24 \) h represented a population that had not received any fresh emissions for several hours and that had aged during the night, mainly due to coagulation. At \( t_p = 48 \) h the particle population was shaped by the aging processes (condensation and coagulation) during the second day, without receiving any fresh emissions.

We then used the particle-resolved populations of the selected plume hours to initialize
individual cloud parcel simulations of a duration of 10 min each. We call the time variable during the cloud parcel stage *cloud parcel time* $t_c$. Since processes other than water vapor condensation and liquid water droplet evaporation were not included in the cloud parcel model simulation, any differences in cloud droplet number concentration and other associated cloud microphysical properties can be exclusively attributed to differences in the aerosol particle population characteristics that was used as input.

### 3.3.2 Set up of Sensitivity Simulations

The purpose of this chapter is to quantify the sensitivity of the errors in calculating cloud microphysical properties due to simplified aerosol mixing state representation to a wide range of environmental conditions. Since the BC mixing state can change due to coagulation with other particles in the population and due to condensation of secondary aerosol species, we performed six 48-hour urban plume simulations that varied in the emission rate of BC-containing particles (100%, 25%, and 2.5% of the case presented *Ching et al.* (2012), denoted by E100, E25, and E10, respectively), and in the number concentration of background particles (100%, and 10% of the case in *Ching et al.* (2012), denoted by B100 and B10, respectively). We call the scenario library formed by these six scenarios M1. The gas phase emissions for all six scenarios in M1 were the same as presented in *Ching et al.* (2012) (denoted by G100). The resulting BC mass concentrations in the M1 scenarios were consistent with observations made in urban and rural areas in the Report to Congress on Black Carbon (*United States Environmental Protection Agency*, 2012). For the base case (B100-E100) we performed two additional urban plume simulations by reducing the emission rate of the gaseous components (50% and 25% of the original case in *Ching et al.* (2012), denoted by G50 and G25, respectively). We refer to these three scenarios of different gas emission rates, (G100, G50 and G25), but with the base-line BC emission and background concentration (B100-E100) as scenario library M2. As we will show in Section 3.4.1, changing these input parameters created a wide range of urban plume conditions where BC aging
proceeded in different ways. The results of M1 are presented throughout this work, and those of M2 are added in Section 3.6.

All other input parameters were identical for the urban plume scenarios. These included the initial chemical composition and the size distribution parameters of background particles and the particle emissions, as well as meteorological conditions such as temperature profile, relative humidity, and mixing height. The base case plume scenario (B100-E100-G100) was described in detail in Ching et al. (2012), and Table 3.1 summarizes the information regarding the background aerosol distributions and the particle emissions.

As outlined in Section 3.3.1 we used four selected aerosol populations from each urban plume scenario as input for the cloud parcel simulations, these were the populations at $t_p = 1\, \text{h}, 12\, \text{h}, 24\, \text{h}, \text{and} 48\, \text{h}$, abbreviated by T1, T12, T24, T48. Since the error sensitivity may also depend on the cooling rate that the aerosol populations is exposed to in the cloud parcel, we explored different cooling rates, $0.15\, \text{K min}^{-1}, 0.5\, \text{K min}^{-1}$ and $0.85\, \text{K min}^{-1}$, denoted by C0.15, C0.5, and C0.85. The three cooling rates correspond to cloud base updraft speeds of $0.55\, \text{m s}^{-1}, 1.82\, \text{m s}^{-1}$ and $3.10\, \text{m s}^{-1}$, respectively, and were selected to represent conditions ranging from stratus (Babb and Verlinde, 1999; Peng et al., 2005) to cumulus cloud types (Lu et al., 2012).

In total this amounts to 96 individual cloud parcel simulations. Table 3.2 provides an overview and lists the abbreviations used for the remainder of this paper to refer to individual cases. For example, the abbreviation B10-E25-G100-T12-C0.15 refers to the cloud parcel simulation with cooling rate of $T' = -0.15\, \text{K min}^{-1}$, and the cloud parcel was initialized with the aerosol population from $t_p = 12\, \text{h}$ using the urban plume run with 10% background aerosol number concentration, 25% BC emission rate and 100% gas emission rate.
<table>
<thead>
<tr>
<th>Initial/Background</th>
<th>( N_a ) / cm(^{-3} )</th>
<th>( D_g ) / µm</th>
<th>( \sigma_g )</th>
<th>Composition by mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aitken mode</td>
<td>1800</td>
<td>0.02</td>
<td>1.45</td>
<td>49.64% ((\text{NH}_4)_2\text{SO}_4) + 49.64% SOA + 0.72% BC</td>
</tr>
<tr>
<td>Accumulation mode</td>
<td>1500</td>
<td>0.116</td>
<td>1.65</td>
<td>49.64% ((\text{NH}_4)_2\text{SO}_4) + 49.64% SOA + 0.72% BC</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Emission</th>
<th>( E_a ) / m(^{-2})s(^{-1} )</th>
<th>( D_g ) / µm</th>
<th>( \sigma_g )</th>
<th>Composition by mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meat cooking</td>
<td>( 9 \times 10^6 )</td>
<td>0.086</td>
<td>1.91</td>
<td>100% POA</td>
</tr>
<tr>
<td>Diesel Vehicles</td>
<td>( 1.6 \times 10^8 )</td>
<td>0.05</td>
<td>1.74</td>
<td>30% POA + 70% BC</td>
</tr>
<tr>
<td>Gasoline Vehicles</td>
<td>( 5 \times 10^7 )</td>
<td>0.05</td>
<td>1.74</td>
<td>80% POA + 20% BC</td>
</tr>
</tbody>
</table>

Table 3.1: Area source strength, \( E_a \), of the three types of emission and the initial/background aerosol population. The initial/background aerosol population size distribution is assumed to be lognormal and defined by the number concentration, \( N_a \), the geometric mean diameter, \( D_g \), and the geometric standard deviation, \( \sigma_g \).

3.4 Overview of Urban Plume and Cloud Parcel Simulations

Section 3.4 presents an overview of the scenario library M1. Section 3.4.1 first summarizes the aerosol characteristics obtained from the six environmental scenarios in M1, which later serve as inputs for the cloud parcel simulations. Section 3.4.2 then presents the results of the cloud parcel simulations initialized by the six environmental scenarios.

3.4.1 Particle Populations under Various Environmental Scenarios

To provide an overview of the range of conditions covered with the six environmental scenarios in M1, we show the time series of the total number and mass concentrations and those of the black-carbon-containing particles in Figure 3.1. In each subfigure the color indicates the level of the BC emissions (magenta for E100, light blue for E25, yellow for E2.5), and the line style indicates the level of background particle concentration (solid for B100,
Table 3.2: Overview of the parameters that were varied to construct a total of 96 cloud parcel simulations, and the corresponding abbreviation used in the text. Urban plume simulations were conducted at two different levels of background particle concentration and three different levels of BC particle emission rates. For the B100/E100 scenario, we conducted two additional runs where the gas emission were varied (G50 and G25). From each of these eight scenarios, four plume hours were chosen to initialize cloud parcel simulations and three different cooling rates were investigated. For example the abbreviation B10-E25-T12-C0.15 refers to the cloud parcel simulation with cooling rate of \( T' = -0.15 \text{ K min}^{-1} \), and the cloud parcel was initialized with the aerosol population from \( t_p = 12 \text{ h} \) using the urban plume run with 10% background aerosol concentration and 25% BC emission rate.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Possible values</th>
<th>Possible values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background particle concentration</td>
<td>B100 100%</td>
<td>B10 10%</td>
</tr>
<tr>
<td>BC particle emission rate</td>
<td>E100 100%</td>
<td>E25 25%</td>
</tr>
<tr>
<td>Gas emission concentration</td>
<td>G100 100%</td>
<td>G50 50%</td>
</tr>
<tr>
<td>Plume hour</td>
<td>T1 1 h</td>
<td>T12 12 h</td>
</tr>
<tr>
<td>Cooling rate (in K min(^{-1}))</td>
<td>C0.15 0.15</td>
<td>C0.5 0.5</td>
</tr>
</tbody>
</table>
dashed for B10). For example, the yellow-dashed line represents scenario B10-E2.5-G100. In Figure 3.1(c) we also show the total aerosol mass concentration for the G50 and G25 scenarios. Note that these scenarios are run only in conjunction with the B100-E100 scenario, i.e. B100-E100-G50 and B100-E100-G25.

The temporal variation of aerosol number concentration $N_a$ in Figure 3.1(a) was governed by particle emission, coagulation and dilution. For all simulations the maximum number concentration was therefore reached at the end of the emission period, at $t_p = 12$ h. It ranged from $1.2 \times 10^3$ cm$^{-3}$ for the least polluted case B10-E2.5-G100 to $1.6 \times 10^4$ cm$^{-3}$ for the most polluted case B100-E100-G100.

Figure 3.1(b) shows the fraction of BC-containing particles. For scenario B10-E100-G100, a scenario of high BC emission rate and low background concentration, more than 95% of all particles contain BC. On the other hand, for the scenario with high aerosol background and the lowest emission rate, B100-E2.5-G100, only up to 11% of particles contain BC.

The total aerosol mass concentration is shown in figure 3.1c. The formation of secondary aerosol material was similar in all G100 cases, since the emissions of gaseous precursors were the same. The total mass concentration on the first day was dominated by ammonium nitrate formation, which evaporated after ammonia emissions ceased (Ching et al., 2012). Secondary production of sulfate and organic mass also occurred on the second day of the simulation. In comparison, less secondary aerosol mass formation was formed in scenarios G50 (orange line), and G25 (purple line). For example, at $t_p=12$ h, $m_a$ is 34.4 µg, 18.5 µg and 16.8 µg for G100, G50 and G25 respectively. The corresponding BC mass concentrations ranged from 0.05 µg m$^{-3}$ to 3.6 µg m$^{-3}$ as shown in Figure 3.1(d). For reference, the concentrations of selected gases are plotted as a function of plume time in Figure S1 in the supplementary material.

To illustrate how the BC mixing state evolved, in Figure 3.2 we show the two-dimensional particle number concentration distribution as a function of dry diameter, $D_{\text{dry}}$, and BC dry mass fraction, $w_{\text{BC, dry}}$ for scenario B100-E100-G100. The BC mass fraction for a particle is
Figure 3.1: (a) Total aerosol number concentration, $N_a$, (b) ratio of BC-containing aerosol number concentration, $N_{a,BC}$ to total aerosol number concentration, $N_a$, (c) total aerosol mass concentration, $m_a$ and (d) total BC-containing aerosol mass concentration, $m_{BC}$, as a function of plume time $t_p$ for the six scenarios in M1. The magenta, blue and yellow represent three black carbon emission rate levels, E100, E25 and E2.5 respectively. The solid and dashed lines stand for two background aerosol number concentration, B100 and B10 respectively. In panel (c), the orange and purple solid lines indicate the total aerosol mass concentration, $m_a$ for the two scenarios in M2, B100-E100-G50 and B100-E100-G25 respectively.
defined as
\[ w_{\text{BC, dry}} = \frac{\mu_{\text{BC}}}{\mu_{\text{dry}}}, \tag{3.2} \]
where \( \mu_{\text{BC}} \) is the BC mass particle and \( \mu_{\text{dry}} \) is the particle’s total dry mass. We define the two-dimensional cumulative number distribution, \( N(D_{\text{dry}}, w_{\text{BC, dry}}) \) as the number concentration of particles that have a dry diameter less than \( D_{\text{dry}} \) and a BC mass fraction less than \( w_{\text{BC, dry}} \). We further define the two-dimensional number distribution, \( n(D_{\text{dry}}, w_{\text{BC, dry}}) \) as
\[ n(D_{\text{dry}}, w_{\text{BC, dry}}) = \frac{\partial^2 N(D_{\text{dry}}, w_{\text{BC, dry}})}{\partial \log_{10} D_{\text{dry}} \partial w_{\text{BC, dry}}}, \tag{3.3} \]

As explained in Section 3.3.1, we focus on four selected plume time snapshots, \( t_p = 1 \text{ h}, 12 \text{ h}, 24 \text{ h}, \text{ and } 48 \text{ h} \). These correspond to the local time of 7am, 6pm, 6am on day 2, and 6am on day 3. In Figure 3.2(a), at \( t_p = 1 \text{ h} \), three distinct horizontal bands represent diesel soot particles with \( w_{\text{BC, dry}} = 70\% \), the gasoline particles with \( w_{\text{BC, dry}} = 20\% \) and meat cooking particles with \( w_{\text{BC, dry}} = 0\% \). Background particles containing trace amounts of black carbon also contributed to the subpopulation at \( w_{\text{BC, dry}} \approx 0\% \) (see Table 3.1).

As the urban plume evolved over the course of the day, particles with BC dry mass fractions ranging between 70% and 0% gradually developed because of condensation of gaseous aerosol precursors and coagulation. In Figure 3.2(b)–(d), at \( t_p = 12 \text{ h} \) and thereafter, the three horizontal distinct bands disappeared since no fresh emissions entered the simulation. For most of the particles \( w_{\text{BC, dry}} \) decreased to less than 60% at \( t_p = 24 \text{ h} \) (Figure 3.2(c)) and to less than 40% after two days (Figure 3.2(d)). The diagonal lines appear because condensation of secondary species decreases BC mass fraction faster for small particles compared to larger particles.

As the BC dry mass fractions of the primary particles decreased, the particles became more hygroscopic. Enhanced hygroscopicity combined with the increase in particle sizes as a result of condensation of gaseous aerosol precursors and coagulation led to decreases in the per-particle critical supersaturations over the course of two days (Ching et al., 2012). At
Figure 3.2: Two-dimensional number concentration distribution $n(D_{\text{dry}}, w_{\text{BC,dry}})$ as function of dry diameter and black carbon dry mass fraction, at (a) $t_p = 1$ h, (b) $t_p = 12$ h, (c) $t_p = 24$ h, and (d) $t_p = 48$ h for environment scenario (B100/E100).
\( t_p = 1 \text{ h}, \) the freshly-emitted particles’ critical supersaturation ranged between 1% and 10%. After two days, most of the particles had critical supersaturation values less than 0.5%.

Changing the BC emission rate, the background aerosol concentration or the gas emission rates impacts the per-particle composition evolution. For the scenarios with reduced BC emission rates, the particles’ BC dry mass fractions decrease faster than for scenario B100-E100-G100. For example, at \( t_p = 24 \text{ h}, \) for scenario B100-E100-G100, 91% of all particles have a BC dry mass fraction less than 30%, while for B100-E2.5-G100, more than 99% of all particles with BC mass fractions less than 30%. This difference in aging of BC particles is because there is less competition among hydrophobic BC particles for coagulation with non-BC particles and condensable gaseous precursors when BC emission is reduced. In contrast, reducing the concentration of background aerosol particles has the opposite effect. At \( t_p = 24 \text{ h}, \) about 70% of particles having dry mass fraction of BC less than 30% for B10-E100-G100. Analogously, reducing gas emission rate from G100 to G25 results in longer persistence of high BC dry mass fractions, for example about 69% of the population have BC mass fractions less than 30% for B100-E100-G25 compared to 91% for B100-E100-G100 at \( t_p = 24 \text{ h}. \)

### 3.4.2 Cloud Parcel Simulations

For an overview of the covered range of conditions in the cloud parcel simulations, Figure 3.3 shows the cloud droplet number concentration, \( N_d, \) versus initial aerosol number concentration, \( N_a. \) This figure displays data from cloud parcel simulations initialized by M1-scenarios.

Triangle, square and circle stand for the three BC emission rates, E100, E25 and E2.5, respectively. Solid and empty shapes represent scenarios B100 and B10, respectively. Blue, green and red colors stand for cooling rates of 0.85 K min\(^{-1}\), 0.5 K min\(^{-1}\) and 0.15 K min\(^{-1}\) respectively (C0.85, C0.5 and C0.15). For example, the green solid triangles refer to simulation B100-E100-G100-C0.5, and there are four of them in Figure 3.3 for the four plume
Figure 3.3: Total cloud droplet number concentration, $N_d$ versus total aerosol number concentration, $N_a$ at $t_p = 1$ h, 12 h, 24 h and 48 h. Blue, green and red represent cooling rates of $0.85 \text{ K min}^{-1}$, $0.5 \text{ K min}^{-1}$ and $0.15 \text{ K min}^{-1}$ respectively. Triangle, square and circle stand for E100, E25 and E2.5 respectively. Filled and empty shapes indicate the background particle concentration, B100 and B10 scenario. For examples, blue solid triangle stands for B100-E100-C0.85 and green empty circle stands for B10-E2.5-C0.5. Symbols of the same color and shape appear four times representing the four selected plume hours, 1 h, 12 h, 24 h and 48 h. There are two black lines, one connecting three solid triangles (B100-E100-G100-T24-C0.15, B100-E100-G100-T24-C0.5 and B100-E100-G100-T24-C0.85), the other connecting another three solid triangles (B100-E100-G100-T1-C0.15, B100-E100-G100-T1-C0.5 and B100-E100-G100-T1-C0.85). The purpose of this is for easy reference when these scenarios are discussed in the text. The blue (B100-E100-G100-T1-C0.85) and green (B100-E100-G100-T1-C0.5) triangles almost overlap with each other.
hours, 1 h, 12 h, 24 h and 48 h. A pair of symbols for the same BC emission rates at two background particle concentrations, B100 and B10 are connected for easier comparison. The solid black lines indicate values of constant activation fractions, $f_N$.

Figure 3.3 shows several expected outcomes. The cloud droplet number concentration $N_d$ increases with increasing aerosol concentration $N_a$. For a given scenario, a stronger cooling rate results in a larger cloud droplet number concentration, $N_d$, and hence larger activated fraction $f_N$. For example, for scenarios B100-E100-G100-T12 (marked with “12 h” on Figure 3.3), $N_d$ increases from about $1.25 \times 10^3 \text{ cm}^{-3}$ (red solid triangle) to $3 \times 10^3 \text{ cm}^{-3}$ (green solid triangle) to $4.3 \times 10^3 \text{ cm}^{-3}$ (blue solid triangle) as the cooling rate increases from C0.15 to C0.5 and to C0.85. The corresponding activation fractions increase from 8% to 19% to 28%. The activated fractions $f_N$ of all the scenarios range approximately between 8% (C0.15) and 90% (C0.85).

However, the sensitivity of $N_d$ to cooling rate depends not only on $N_a$, but also on the underlying particle population characteristics. For example, the total aerosol number concentration for B100-E100-G100-T1 and B100-E100-G100-T24 are approximately the same, (marked with “1 h” and “24 h” on Figure 3.3), however the effect of cooling rate on cloud droplet number concentration is smaller for $t_p=1 \text{ h}$ than that for $t_p=24 \text{ h}$. This is because the aerosol population at $t_p=1 \text{ h}$ mostly consists of freshly emitted gasoline soot and diesel soot particles, which are hydrophobic, and this leads to limited the enhancement in $N_d$ when comparing the C0.15 and the C0.85 scenario. On the other hand, the particle population at $t_p=24 \text{ h}$, contains aged BC-containing particles and hygroscopic background particles. Such a population is on the whole more CCN-active, and is more sensitive to any change in the cooling rate of the parcel.

For most scenarios, reducing the concentration of background aerosol leads to a reduction in $N_d$ (compare corresponding filled and empty symbols connected by the straight line). The associated reduction in $N_a$ is even larger, hence the activation fraction increases. A notable exception are the scenarios at $t_p=12 \text{ h}$ (marked with 12 h on Figure 3.3). For these scenarios,
\( N_d \) increases for the B10 simulations compared to B100 for all three cooling rates. This is due to the interaction of the difference in the two CCN spectra (B10 and B100) and the response of maximum saturation vapor ratios to such difference, which will be explained in detail in Section 3.5.2. The numerical values of \( N_d \) for all the scenarios in library M1 are listed in Table C.1 in the appendix to this chapter.

In summary, changes in background aerosol concentration, BC emission rates and gas emission rates modify the underlying urban plume dynamics, which results in different CCN properties of the aerosol population. To determine how these differences in CCN properties translate to the corresponding differences in cloud droplet number concentration, the maximum supersaturation ratio, \( S_{\text{max}} \), attained in the parcel simulation is the critical factor, which in turn depends on aerosol population properties and the cloud parcel cooling rate. In the next section, we will examine how the difference in \( N_d \) for any two environmental scenarios can be attributed to changes in the plume properties versus changes in the cloud parcel response.

### 3.5 Plume Effect and Parcel Effect

Changing BC emission rates, the aerosol background concentration, or gas emission rates can modify the aerosol CCN spectrum in the urban plume. However, given a certain cooling rate, this only partially explains the subsequent change in cloud droplet number concentration, because the maximum supersaturation in the cloud parcel changes accordingly in response to the altered aerosol population. In this section we develop a framework to disentangle these two factors (Section 3.5.1), so that we can attribute differences in cloud droplet number concentration between two scenarios to differences in the underlying aerosol population (“plume effect”) or to differences in the supersaturation response (“parcel effect”). We then apply the framework to compare scenarios with different aerosol background concentration (Section 3.5.2), and with different black carbon emission rates. (Section 3.5.3).
3.5.1 Definition of Plume Effect and Parcel Effect

To attribute the difference in $N_d$ between any two different environmental scenarios to the differences in the shapes of the corresponding CCN spectra of the underlying aerosol populations and to the maximum saturation ratios, $S_{\text{max}}$, achieved in the parcel simulations, we introduce the quantities as shown schematically in Figure 3.4. The two CCN spectra correspond to aerosol populations from two different urban plume scenarios. When used as input for the cloud parcel simulations they yield the maximum supersaturations $S_{\text{max},1}$ and $S_{\text{max},2}$, respectively, and the intersections with the CCN spectra represent the resulting cloud droplet number concentrations, $N_{d,1}$ and $N_{d,2}$. Here we assume that particles with critical supersaturation lower than $S_{\text{max}}$ activate and become cloud droplets. This neglects kinetic limitation effects on cloud droplet growth (Chuang et al., 1997; Nenes et al., 2001).

To decompose the difference in cloud droplet number concentration between two scenarios, $\Delta N_d = N_{d,2} - N_{d,1}$, into a plume and a parcel component, it is useful to define $N_{d,3}$ as the cloud droplet number concentration for environmental scenario 2 if the maximum saturation ratio attained is $S_{\text{max},1}$, and $N_{d,4}$ as the cloud droplet number concentration for environmental scenario 1 if the maximum saturation ratio is $S_{\text{max},2}$. We then rewrite $\Delta N_d$ as follows:

$$
\Delta N_d = N_{d,2} - N_{d,1}
= \frac{1}{2}(N_{d,2} - N_{d,3} + N_{d,3} - N_{d,1}) + \frac{1}{2}(N_{d,2} - N_{d,4} + N_{d,4} - N_{d,1})
= \frac{1}{2}(N_{d,2} + N_{d,3}) - \frac{1}{2}(N_{d,1} + N_{d,4}) + \frac{1}{2}(N_{d,2} + N_{d,4}) - \frac{1}{2}(N_{d,1} + N_{d,3})
= \Delta N_{d,\text{plume}} + \Delta N_{d,\text{parcel}}
$$

As seen in Figure 3.4, $\Delta N_{d,\text{plume}}$ can be understood as the difference in $N_d$ calculated using the CCN spectra of scenario 1 and 2 at the average of $S_{\text{max},1}$ and $S_{\text{max},2}$. Similarly, $\Delta N_{d,\text{parcel}}$ is the difference in $N_d$ calculated with an averaged CCN spectrum of the two
scenarios at $S_{\text{max},1}$ and $S_{\text{max},2}$.

We further define the plume effect, $\alpha = \frac{\Delta N_{d,\text{plume}}}{|\Delta N_d|}$ and parcel effect, $\beta = \frac{\Delta N_{d,\text{parcel}}}{|\Delta N_d|}$. In this way, $\alpha + \beta = 1$, when $N_{d,2}$ is greater than $N_{d,1}$, and $\alpha + \beta = -1$ when $N_{d,2}$ is smaller than $N_{d,1}$. A positive value for $\alpha$ implies that the plume effect increases $N_d$, and a positive value for $\beta$ means that the parcel effect increases $N_d$. The larger the magnitudes of $\alpha$ or $\beta$, the stronger is the corresponding effect on $\Delta N_d$. One should note that in our analysis, $\Delta N_d$ is non-zero, permitting the devising of such pair of metrics.

Comparing any two scenarios, we observe that the plume effect is large when the maximum saturation ratios occur at values for which the two CCN spectra differ significantly. On the other hand, the parcel effect is large, when the shift in the maximum saturation ratios
is found where the slope of the CCN spectrum is steep.

### 3.5.2 Plume Effect and Parcel Effect for Changes in Aerosol Background Concentration

We exemplify this concept in Figure 3.5 by comparing the CCN spectra for the two aerosol background scenarios B100 (solid line) and B10 (dashed line) at \( t_p = 1 \) h, 12 h, 24 h and 48 h (rows) and for the three BC emission scenarios E100, E25, and E2.5 (columns). The vertical solid and dashed lines indicate the maximum supersaturations attained in the cloud parcel simulations initialized by the two different urban plume scenarios, B100 and B10, respectively. The three pairs of solid and dashed vertical lines, from left to right in each panel in the Figure 3.5, represent the values of maximum supersaturations attained for the cooling rates of C0.15, C0.5 and C0.85 respectively.

The CCN spectra for \( t_p = 1 \) h, are representative of populations that contain a hygroscopic and a hydrophobic subpopulation (indicated by flat section around 0.3% and the steep section around 1%), consistent with Figure 3.2(a). At \( t_p = 12 \) h, 24 h and 48 h, a larger fraction of particles has lower critical supersaturation. The CCN concentrations are generally largest for \( t_p = 12 \) h, at the end of the emission period. For the same reason, the differences in CCN concentrations between scenarios E100, E25, and E2.5 are the largest for \( t_p = 12 \) h. Furthermore, the highest CCN concentrations for \( t_p = 12 \) h coincide with lowest values of maximum supersaturation due to the competition of the particles for water vapor.

We apply the framework described in Section 3.5.1 to attribute the difference in \( N_d \) between two scenarios of the same BC emission and same gas emission rate (G100) but different aerosol background concentration to plume effect and parcel effect.

The columns in Figure 3.6 show the comparisons at 100%, 25% and 2.5% BC emission rate, respectively. The panels along a row show the results at the same cooling rate. The dark colored bars represent the plume effect \((\alpha)\), and the pale colored bars represent the
Figure 3.5: CCN spectra at the four selected plume hours are shown along four separate rows. The columns represent scenarios with different BC emission rates. The solid lines are the scenarios B100, the dashed lines are the scenarios B10.
Figure 3.6: Comparison of plume effect and parcel effect when changing the aerosol background concentration. The four bars in each panel are for $t_p = 1$ h, 12 h, 24 h and 48 h. Pale color and dark color bar represents parcel and plume effects, respectively. The sign on top of each bar gives the sign of the overall change in $N_d$. Positive means $N_d$ at lower background concentration environment is larger than that at higher background environment.

The plume effect is negative for all scenarios in Figure 3.6 as illustrated by negative dark colored bars. This is consistent with Figure 3.5, which shows that the CCN spectra for the B10 simulations (dashed lines) are below the spectra for the B100 simulations (solid line), i.e. reducing background aerosol concentrations leads to a decrease in CCN concentrations. However, simultaneously, the parcel effect is positive for all the scenarios, i.e. the
maximum supersaturation for the B10-simulations reaches higher values compared to the B100-simulation due to reduced water vapor competition. Hence, the plume and parcel effects for the scenarios shown in Figure 3.6 counteract each other, which exemplifies the buffering mechanism in the cloud droplet formation process \((\text{Stevens and Feingold, 2009})\). The overall change in \(N_d\) is determined by the competition between the plume and parcel effect. For most scenarios \(N_d\) decreases when the background aerosol concentration is reduced. Further, most scenarios with a reduction in \(N_d\) show plume effects with values close to \(-1\). For these cases \(\Delta N_d\) can be mainly attributed to changes in the underlying aerosol population, while the contribution of \(\Delta N_d\) from the change in maximum supersaturation is small. However, for example in the case B100-E25-G100-T12-C0.15 versus B10-E25-G100-T12-C0.15, the magnitudes of both plume and parcel effects are close to each other and larger than those for the other cases. This indicates that both effects contribute significantly in changing \(N_d\), and are in closer counteraction with each other compared to those scenarios with dominant negative plume effects.

Interestingly, two scenarios show an overall enhancement in \(N_d\) when the background aerosol concentration is reduced, they are B100-E100-G100-T12-C0.5 versus B10-E100-G100-T12-C0.5 and B100-E100-G100-T12-C0.15 versus B10-E100-G100-T12-C0.15. Detailed process analysis to understand this counterintuitive result yields that while the hygroscopic background aerosol particles are good CCN, they also act as a sink for secondary aerosol mass, hence reducing background aerosol concentration can increase the CCN activity of fresh BC-containing particles. The latter effect occurs for \(t_p = 12\) h, and the CCN spectra of B100-E100-G100 and B10-E100-G100 end up very close to each other as shown in Figure 3.5. For these cases the positive parcel effect dominates over the negative plume effect, and \(N_d\) increases despite the fact that the background aerosol concentration is reduced.

Based on the above discussion, when reducing the aerosol background concentration, \(N_d\) decreases, and such decrease can be almost exclusively attributed to a negative plume effect. There are a few interesting exceptions, where the negative plume effect is overcompensated
by a positive parcel effect. This then leads to the counterintuitive result that $N_d$ increases when decreasing the background aerosol concentration.

### 3.5.3 Plume Effect and Parcel Effect for Changes in Black-Carbon Emission

Next we compare the scenarios with different BC emission rates while keeping the same background particle concentrations. Overall, we found that when reducing BC emissions, $N_d$ decreases for most of the scenarios. Two pronounced features regarding the attribution of $\Delta N_d$ to plume and parcel effects can be seen from Figure 3.7. First, using the populations from plume hour $t_p = 1$ h gives qualitatively different results compared to the results at other time snapshots. Second, for the weaker cooling rate, $0.15 \text{ K min}^{-1}$, the plume and parcel effects interact differently than what we observe at stronger cooling rates, $0.5 \text{ K min}^{-1}$ and $0.85 \text{ K min}^{-1}$. In several scenarios at $0.15 \text{ K min}^{-1}$, the plume and parcel effects act in the same direction in changing $N_d$, instead of counteracting each other or dominating one another.

The shapes of CCN spectra of the corresponding scenarios and the associated maximum saturation ratios attained in the parcel elucidate the wide range of patterns of plume and parcel effects interactions and the resulting $\Delta N_d$ observed in Figure 3.7. Figure 3.7 shows only the results of the comparison between E100 and E25 at two background concentration environments, B100, and B10. The comparison between E25 and E2.5 show a similar behavior compared to the comparisons between E100 and E25.

Regarding the behavior at $t_p = 1$ h, the CCN spectra for B100-E100-G100 and B100-E25-G100 at $t_p = 1$ h are very close to each other over the relevant range of supersaturations (Figure 3.8). This is because at this time the population consists mostly of background particles, while BC particles are in the minority. Consequently this causes only a slight difference in $S_{\text{max}}$ and the difference in cloud droplet number concentration, $\Delta N_d$, is either positive
Figure 3.7: Same as 3.6, with the bars showing the plume effect and parcel effect for the change in cloud droplet number concentration, $N_d$, comparing scenarios of different black-carbon emission with the same amount of background particle concentration.
or negative depending on how sensitive the CCN spectra are to those slightly different $S_{\text{max}}$ values. The same interpretation can be applied to B10-E100-G100 and B10-E25-G100. In contrast, the CCN spectra for populations under the two different BC emission rates at the other three plume hours are more distinguishable from each other, this is because in those cases, the emissions have been in effect for a longer period of time.

The second feature can be understood as follows. Referring to Figure. 3.8, although the CCN spectra of E100 lies above that of E25 at the parcel maximum supersaturation values, the supersaturation achieved in E100 is larger than that achieved in E25. This is counterintuitive and is due to the fact that the CCN spectrum for E100 is lower than that of E25 for critical supersaturation values less than 0.07%. This implies there are more CCN-active particles in the BC emission rate reduced environment (E25), and this leads to smaller maximum supersaturation values achieved in E25, hence negative parcel effect. This cooperates with the negative plume effect originating from the lower total particle concentrations under E25 than under E100, results in concurrent negative plume and parcel effects on $N_d$ observed in some plume hours shown.

In summary, the plume and parcel effects are formulated to quantitatively attribute the change in cloud droplet number concentration to the change in the underlying shape of CCN spectrum (plume effect) and to the change in parcel supersaturation (parcel effect). This analysis reveals the complex nature of the interaction between the CCN spectral shape and the response of parcel supersaturation to the water vapor competition among particles of different mixing state. Reducing hydrophilic background particles generally leads to a negative plume effect; while reducing BC particles can result in a variety of outcomes regarding plume and parcel effects: same direction, opposite direction, or one being dominant over the other.
Figure 3.8: CCN spectra at the four selected plume hours are shown along four separate rows. Along each row, the two panels show the comparison of two CCN spectra for two different BC emission, E100 (magenta) versus E25 (blue), at two background concentration environments, B100 and B10.
3.6 Error in Cloud Microphysical Properties Due to Simplified Aerosol Mixing State Representation

To quantify the importance of aerosol mixing state for predicting cloud microphysics quantities, we compare the particle-resolved cloud parcel simulations as presented in Section 3.4 to simulations where we average the composition of the input aerosol population within 25 prescribed size bins before performing the cloud parcel simulation. The particles are placed according to their dry diameters, using 25 size bins ranging from $10^{-4}$ to $10 \mu m$ uniformly logarithmically spaced. For details regarding how to derive the composition-averaged aerosol population, readers are referred to Ching et al. (2012) and Chapter 2 of this dissertation.

We construct such a “composition-averaged” cloud parcel input from all urban plume scenarios and evaluate the differences between particle-resolved reference case and composition-averaged case for five cloud microphysics quantities, namely cloud droplet number fraction, the mass fraction of BC that is nucleation-scavenged, effective radius, relative spectral dispersion, and albedo. We define error for quantity $X$ as follows,

$$\Delta X = \frac{X_{\text{comp}} - X_{\text{ref}}}{X_{\text{ref}}},$$

(3.4)

where $X_{\text{comp}}$ and $X_{\text{ref}}$ are values of quantity $X$ calculated with composition-averaged and particle-resolved aerosol populations respectively.

We compare the effective radii calculated from particle-resolved model to the ones calculated from composition-averaged particle populations input in Section 3.6.2. Since effective radius is an important microphysical quantities for evaluating cloud radiative forcing (Benguier et al., 2000; Liu and Daum, 2002; Feingold et al., 2003; Feingold, 2003; Twohy et al., 2005), we further calculate and compare the two corresponding cloud shortwave albedos from these two calculated effective radii. Following the presentation of the error in relative spectral dispersion, the section concludes with a comparison between the effective radii.
calculated by particle-resolved model and by parameterization with cloud droplet spectral dispersion suggested by Liu and Daum (2002).

3.6.1 Error in Cloud Droplet Nucleation and Black Carbon Nucleation Scavenging

To visualize how the error in a quantity depends on the chosen scenario, we display the results as shown in Figures 3.9–3.12. In these figures, the upper four panels, (a)–(d), show the error for the quantity of interest for all G100 scenarios as a function of cooling rate (abscissa) and BC emission rate (ordinate) at four selected plume hours, \( t_p = 1 \) h, \( t_p = 12 \) h, \( t_p = 24 \) h and \( t_p = 48 \) h respectively. The two simulations at different levels of aerosol background concentrations for the same BC emission rate and cooling rate are shown by two dots next to each other, with the upper left one for B100 and the lower right one for B10. The lower four panels, (e)–(h), show the error for the B100-E100 scenarios, now stratified by cooling rate and gas emission rate, for the same four selected plume hours.

Figure 3.9 shows that composition-averaging generally results in overestimating the cloud droplet number fraction \( f_N \). Comparing the four different plume times, the overestimation in \( f_N \) is largest for \( t_p = 1 \) h, reaching a maximum of 45% for B10-E100-G100-T1-C0.5 (Figure 3.9). This is because at this time the population consists of two distinct subpopulations, namely freshly emitted hydrophobic black carbon particles and hygroscopic background particles as we see in Figure. 3.2(a) that three horizontal patterns indicate respectively the black carbon containing emission (diesel and gasoline soot emission at \( w_{BC, dry} = 70\% \) and \( 20\% \) respectively) and hygroscopic background particles \( (w_{BC, dry} \sim 0\%) \). Composition-averaging results in the hydrophobic aerosol particles being artificially mixed with hygroscopic material, and hence some aerosol particles can activate that would not activated in the particle-resolved reference calculation. At later plume hours (Figures 3.9(b)–(d)), some aging of the BC-containing particles has taken place, and the artificial mixing has less impact on
$N_d$, hence $\Delta f_N$ decreases. However, the details of this aging process in the urban plume play a role. For example, at $t_p = 24\,\text{h}$, the errors in $f_N$ are larger than those at $t_p = 12\,\text{h}$ and $48\,\text{h}$. This is due to evaporation of ammonium nitrate towards the end of the first day (Figure 2.1(d)), reversing the aging process to some extent.

Figures 3.9(e)–(h) show that the error in $f_N$ for the G50 and G25 scenarios are larger than for the G100 simulations. The maximum error in $f_N$ attains 11% for all the scenarios of G100, while it reaches 22% and 35% for those of G50 and G25 respectively. When the gas emission rates are reduced less condensable secondary aerosol mass is produced, so the aerosol aging process is slowed down and larger errors persist for a comparatively longer time. From the overview in Figure 3.9 it also becomes obvious that $\Delta f_N$ does not show any simple relationship with cooling rate, black carbon emission rate or background particle concentration. This is consistent with the finding in Ching et al. (2012).

Figure 3.10 shows the errors in nucleation scavenged BC mass fraction. The color bar is plotted in logarithmic manner since the error in $f_{BC}$ spans three orders of magnitude. There are four scenarios having slightly negative error in $f_{BC}$, which are indicated by empty circles in Figure 3.10. The errors in $f_{BC}$ are largest for $t_p = 1\,\text{h}$, ranging between 21% and 1022% for all the environmental scenarios presented here, and gradually decrease for larger plume times. For example, at $t_p = 12\,\text{h}$, the errors range only from 6% to 58%.

Comparing the magnitudes of $\Delta f_N$ to $\Delta f_{BC}$, we see that different patterns exist between them. Small error in $f_N$ does not necessarily imply small error in $f_{BC}$, and this is consistent with the findings in Ching et al. (2012). The reason is that composition-averaging distorts the mixing state information. Even if the cloud droplet number concentrations are the same in particle-resolved and composition-averaged calculations, the composition of the particles may differ substantially, which leads to larger errors in $\Delta f_{BC}$.

In summary, for all scenarios investigated, $\Delta f_N$ is within range of 25%, except for $t_p = 1\,\text{h}$ when the largest errors ($\sim 45\%$) occur for aerosol populations that contain externally mixed hydrophobic and hygroscopic subpopulations. For $\Delta f_N$, there is no clear dependence on
Figure 3.9: Error for activation fraction, $f_N$, due to simplified aerosol mixing state model representation. Note that the maximum error in $f_N$ is 45% and occurs for B100-E100-G100-C0.5-T1. To increase the color resolution of the color bar, the scale is capped at 20%.
Figure 3.10: Error in black carbon nucleation scavenged fraction, $f_{BC}$, due to simplified aerosol mixing state model representation. Since the error in $f_{BC}$ spans three order of magnitude, the magnitude of errors are shown in logarithmic scale. The four empty circles represent negative error in $f_{BC}$, and they are all slightly negative of at most $-0.1\%$.  

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cooling rate, aerosol background and BC emission, while $\Delta f_N$ is larger when gas emission rate is lower. $\Delta f_{BC}$ is larger than $\Delta f_N$ for the first 1.5 days, while in the end of the second day, it is less than $\Delta f_N$. Broadly speaking, $\Delta f_{BC}$ decreases with increasing cooling rate, and is larger when gas emission rate is lower.

### 3.6.2 Error in Effective Radius and Dispersion

Section 3.6.1 discussed cloud microphysics bulk quantities. In this section we turn to quantities related to the cloud droplet spectrum, namely effective radius, $r_{\text{eff}}$ and dispersion, $\epsilon$. After we present the quantification of errors in $r_{\text{eff}}$ and $\epsilon$ introduced by composition-averaging, we discuss the implication of the errors in $r_{\text{eff}}$ for cloud albedo and radiative forcing.

The effective radius of a cloud droplet size spectrum is defined as the ratio of the third statistical moment to the second statistical moment of the cloud droplet spectrum. Since we define the cloud droplets to be particles with wet diameter greater than 2 $\mu$m, the effective radius can be written as the following,

$$r_{\text{eff}} = \frac{\int_{2 \mu m}^{\infty} r^3 n(r) dr}{\int_{2 \mu m}^{\infty} r^2 n(r) dr}.$$  \hspace{1cm} (3.5)

The spectral dispersion of the cloud droplet spectrum is defined as the ratio of the standard deviation of the cloud droplet spectrum to the average diameter of the droplet population.

$$\epsilon = \frac{\sigma(D)}{\overline{D}}.$$ \hspace{1cm} (3.6)

The results for $t_p = 1$ h, 12 h, 24 h and 48 h are shown in Figure 3.11 for $\Delta r_{\text{eff}}$, and in Figure 3.12 for $\Delta \epsilon$. The error in $r_{\text{eff}}$ ranges between +4% and −12%, and the error in $\epsilon$ ranges between +60% and −30% As seen in Figure 3.11 and Figure 3.12, there is no simple pattern of how the environmental conditions influence $\Delta r_{\text{eff}}$ and $\Delta \epsilon$. In other words, no
particular set of environmental conditions is favoring small or large error in $r_{\text{eff}}$ and $\epsilon$. The magnitudes of $\Delta r_{\text{eff}}$ (Table C.8) are approximately $-1/3$ of the corresponding magnitudes of $\Delta f_N$ (Table C.6), which is consistent with the findings in Ching et al. (2012) (Chapter 2).

Slingo (1990) suggested that an accuracy of 5% in cloud microphysical quantities such as effective radius and cloud droplet number concentrations is required to simulate the impact of cloud microphysical quantities on climate. The errors in cloud microphysical quantities found in this dissertation due to aerosol mixing state simplified representation are therefore significant and relevant.

We further examine the error in shortwave upward radiative flux caused by the error in effective radius, $r_{\text{eff}}$ for the different environmental scenarios. We performed simulations using the shortwave rapid radiative transfer model, RRTM_SW (version 2.5), (Mlawer et al., 1997; Mlawer and Clough, 1997, 1998) to obtain the shortwave upward radiative flux imposed by clouds composed of a wide range of effective radii. The ranges of effective radii input to RRTM_SW are the same as those obtained in the environmental scenarios M1 and M2. Two sets of simulations were performed, one assumed liquid water path of 50 g m$^{-2}$, another assumed 100 g m$^{-2}$. We found that for the maximum underestimation in effective radius of $-12.25\%$ and the maximum overestimation of $+4.58\%$ (refer to Section 3.6.2 and Figure 3.11), the errors in shortwave upward radiative flux are $+3.96\%$ and $-1.13\%$ respectively at liquid water path of 50 g m$^{-2}$, and $+3.22\%$ and $-0.79\%$ at liquid water path of 100 g m$^{-2}$. For example at liquid water path of 50 g m$^{-2}$, the corresponding magnitude of errors in shortwave upward radiative flux, ranging between $-3.42$ W m$^{-2}$ and $+12.12$ W m$^{-2}$, is significant compared to the net radiative flux due to carbon dioxide doubling (Slingo, 1990).

3.6.3 Parameterization of Effective Radius

A number of parameterizations have been proposed in previous studies to express the effective radius in terms of liquid water content and cloud droplet number concentration Martin et al.
Figure 3.11: Error in effective radius of cloud droplet size spectrum, $r_{\text{eff}}$, due to simplified aerosol mixing state model representation. 
Figure 3.12: Error in relative spectral dispersion of cloud droplet size spectrum, $\epsilon$, due to simplified aerosol mixing state model representation.
One parameterization that is widely used is as follows,
\[ r_{\text{eff}} = \beta \left( \frac{L}{N_d} \right)^{1/3} . \]  

(3.7)

Based on aircraft data, Martin et al. (1994) determined the prefactor \( \beta \) as 1.08 for marine cloud and 1.14 for continental cloud. McFarquhar and Heymsfield (2001) concluded from their analysis of the INDOEX campaign that the effective radius obeys the Equation (3.7) with \( \beta = 1.06 \) for pristine clouds, and \( \beta = 1.11 \) for polluted clouds. McFarquhar and Heymsfield (2001) and Lu and Seinfeld (2006) also pointed out that \( \beta \) depends on skewness and dispersion of the cloud droplet spectrum and suggested to parameterize \( \beta \) as a function of spectral dispersion of the cloud droplet spectrum. Pontikis and Hicks (1992); Liu and Daum (2000, 2002). Liu and Daum (2002) showed that without taking into account this dispersion effect, the effective radius may be underestimated and the associated aerosol first indirect effect may be consequently overestimated. Here we compare the effective radius calculated with the particles resolved model results to the one parameterized using Liu and Daum (2002), in which \( \beta \) is given as
\[ \beta = \frac{(1 + 2 \epsilon^2)^{2/3}}{(1 + \epsilon^2)^{1/3}} , \]  

(3.8)

where \( \epsilon \) is the relative spectral dispersion of the cloud droplet spectrum.

We use the values of liquid water content, \( L \), cloud droplet number concentration, \( N_d \) and cloud droplet spectral dispersion, \( \epsilon \) from the particle-resolved cloud parcel simulations for Eq. (3.7) and (3.8) to calculate the parameterized effective radius, \( r_{\text{eff}}^{\text{para}} \), then compare it to the one computed directly from particle-resolved cloud parcel simulations according to Eq. (3.5).

From the results of the comparison, \( \Delta r_{\text{eff}} = \frac{r_{\text{eff}}^{\text{para}} - r_{\text{eff}}}{r_{\text{eff}}} \), we see in Figure 3.13 that the error of the parameterization is very small. It overestimates \( r_{\text{eff}} \) by at most 0.5% for all of the scenarios, where a dependence on cooling rate can be observed (largest overestimation...
occurs for the weakest cooling rate).

### 3.7 Summary and Conclusion

This chapter explored the sensitivity of the impacts of BC mixing state on cloud microphysical parameters to environmental conditions. We created a range of particle-resolved aerosol initial conditions by developing a scenario library of eight 48-h urban plume scenarios that varied in BC emission rates, aerosol background concentration, and gas emission rates. Particle-resolved cloud parcel simulations were then initialized using the particle-resolved output of the eight plume scenarios at four selected plume hours and were performed using three different cooling rates. This resulted in 96 (8 × 4 × 3) cloud parcel simulations.

Reducing BC emission rates or aerosol background concentrations led to a decrease in the cloud droplet number concentration for most scenarios. Detailed process-level analysis revealed that this reduction could be attributed to a dominant negative plume effect that was only partially offset by a positive parcel effect. There were notable exceptions, in that $N_d$ increased when background concentration was reduced (e.g. B100-E100-G100-T12-C0.5), and this happened because the background aerosol particles also play the role as a sink for secondary aerosol mass. Reducing background aerosol concentration, would lead to increase in CCN activity of the emitted BC particles.

The second focus of this chapter was to quantify the error in aerosol activation fraction, black carbon nucleation-scavenged mass fraction, effective radius and relative spectral dispersion caused by simplified aerosol composition representation in the model. The errors in activation fraction was within 25% for the scenarios that used the populations at $t_p = 12, 24,$ and 48 h as initial aerosol populations. Overpredictions in $f_N$ were more prevalent. Using the populations at $t_p = 1$ h led to larger errors (up to 45%), because they contained a subpopulation of fresh BC particles, which were artificially aged by the composition-averaging procedure. This is consistent with the findings in (Ching et al., 2012). Errors in activation
fraction tended to be larger for the scenarios with reduced gas emission rates, since for these scenarios less secondary aerosol mass was produced, hence the aging process was slowed down. One might have expected to observe smaller errors with larger cooling rates, however this was not confirmed by the results.

Composition-averaging resulted generally in an overprediction of the nucleation-scavenged BC mass fraction. This overprediction was largest for the scenarios using \( t_p = 1 \) as initial aerosol population (up to 1347%), and increased for reduced gas emission rates. In contrast to the error in activation fraction, the error in nucleation-scavenged mass fraction did show a decrease with cooling rate.

For both effective radius and relative dispersion the dependence of errors on environmental conditions does not show a clear pattern. For effective radius the errors were within 12% for all scenarios. Underpredictions in \( r_{\text{eff}} \) are more prevalent. In the environments with reduced gas emissions, the values for \( \Delta r_{\text{eff}} \) are larger. The corresponding errors in short-wave upward radiative flux found from RRTM_SW simulations are about +4 % and −1 % respectively for the largest underestimated and overestimated effective radii at liquid water path of 50 g m\(^{-2}\).

The error in dispersion, \( \Delta \epsilon \) ranges between +60% and -30% for the range of environmental scenarios investigated. 3D cloud-resolving modeling studies with Lagrangian microphysical framework by Bewley and Lasher-Trapp (2011) and Cooper et al. (2013) found that the cloud droplet number size distribution is broader by an order of magnitude when entrainment is taken into account. Compared to the effect of entrainment on spectral dispersion of cloud droplet spectra, the error introduced by simplified aerosol mixing state representations is less significant.

The errors in cloud microphysical quantities found in this dissertation due to aerosol mixing state simplified representation are significant and climate-relevant when examining the impact of these quantities on climate as suggested by Slingo (1990) that an accuracy of 5% in cloud microphysical quantities is required.
We concluded with a comparison of effective radii obtained from particle-resolved calculation and from a parameterization suggested by Liu and Daum (2002) using relative dispersion. Errors in $r_{\text{eff}}$ originating from simplified aerosol composition representation are larger than the ones cause by using the parameterization, provided that the $N_d$, $\epsilon$ and liquid water content are accurately known and as input parameters for the parameterization.

Jacobson (2002) and Bond (2007) proposed that the control of black carbon emission from fossil fuel could be an effective way of mitigating global warming in the short term. The rationale behind this is that black carbon absorbs solar radiation, resulting in a warming impact on climate, but due to the short life time of BC, BC emission reductions would quickly lead to a reduction in the burden of BC.

When considering the cooling from the aerosol indirect effect that black carbon particles have after becoming hygroscopic through atmospheric aging processes, Bahadur et al. (2012) found that cloud droplet number concentration decreases by 6% to 9% for 50% reduction in black carbon particle concentration. Our results show that the reduction in BC emission rates results in a wide range of changes in cloud microphysical properties, including $N_d$ and $r_{\text{eff}}$ depending on the environmental conditions. Reduction in BC emission leads to decrease in $N_d$ and increase in $r_{\text{eff}}$ are found in most of the scenarios presented here. This supports the conjecture by Chen et al. (2010) that reducing black carbon emission can suppress the aerosol indirect effect with larger cloud droplets and hence lower albedo.

However, a recent review by Bond et al. (2013) provides a comprehensive summary of the diverse effects that black carbon particles have on climate, and states that the effects of reducing black carbon number concentration could either increase or decrease CCN concentration. In fact we see this dual role of black carbon particles in our results: When the majority of black carbon particles are aged by hydrophilic material (later plume hours in our simulations), reducing them results in reducing CCN and cloud droplet number concentration. In contrast, for a population containing freshly emitted particles (early plume hours in our simulations), reducing BC emission can enhance cloud droplet number concentration.
Figure 3.13: Error in effective radius of cloud droplet size spectrum, $r_{\text{eff}}$, due to parameterization suggested by Liu and Daum (2002)
Chapter 4

Relative spectral dispersion of cloud droplet size spectra

This chapter investigates the factors that determine the relative spectral dispersion of the cloud droplet spectrum, and explores the relationship between the relative dispersion and the mixing state of the underlying aerosol population. The analysis is based on the results from the scenario library M1 established in Chapter 3. This chapter is prepared as a journal article for publication in the Journal of Geophysical Research. The methodology section of this chapter has been shortened compared to the prepared manuscript to avoid repetition.

4.1 Introduction

Aerosol particles are ubiquitous in the atmosphere. They alter the Earth’s energy budget by absorbing and scattering solar and terrestrial radiation (Charlson et al., 1992) which is known as the direct effect of aerosol particles on climate. Twomey (1974, 1977) suggested that when the aerosol particle number concentration increases, the number concentration of CCN increases, and assuming constant amount of liquid water, the size of individual droplet decreases. The cloud reflectivity is thus enhanced, which results in a cooling effect on climate, referred to as the indirect effect of aerosol particles on climate.

Many cloud radiative properties such as optical depth and single scattering albedo are functions of effective radius, $r_{\text{eff}}$, which is defined as the ratio of the third moment to the second moment of the cloud droplet spectrum. In global climate models the effective radius
is parameterized by the cloud liquid water content and cloud droplet number concentration
(Pontikis and Hicks, 1992; McFarquhar and Heymsfield, 2001; Peng and Lohmann, 2003). The cube root of the ratio of the liquid water content to the droplet number concentration gives the mean volume radius \( r_v \), which is then scaled by a factor to give effective radius \( r_{\text{eff}} \).

Martin et al. (1994) presented aircraft observations demonstrating that the cube of the effective radius is proportional to the cube of the mean volume radius, \( r_v \)

\[
\frac{3}{3} r_{\text{eff}} = \alpha r_v^3, \tag{4.1}
\]

where

\[
r_v = \left( \frac{3L}{4\pi \rho_w N_d} \right)^{\frac{1}{3}}, \tag{4.2}
\]

\( L \) is the liquid water content and \( N_d \) is the cloud droplet number concentration. Martin et al. (1994) proposed that \( \alpha = 0.80 \pm 0.07 \) and \( 0.67 \pm 0.07 \) for continental and maritime air masses, respectively. From INDOEX observations, McFarquhar and Heymsfield (2001) also concluded that the effective radius is proportional to the cube root of the mean volume radius, and the suggested that \( \alpha = 0.83 \pm 0.07 \) and \( 0.73 \pm 0.08 \) for aerosol number concentration, \( N_a < 500 \text{ cm}^{-3} \) and \( N_a > 1500 \text{ cm}^{-3} \), respectively. Liu and Daum (2002) argued that the effective radius is not accurately parameterized without considering the spectral shape of the cloud droplet spectrum. They suggested that rather by a constant, the volume mean radius should be multiplied by a coefficient, \( \beta \), which is a function of spectral dispersion, \( \epsilon \), defined as the ratio of the standard deviation of the cloud droplet spectrum to the average radius of the droplets.

\[
r_{\text{eff}} = \beta r_v \tag{4.3}
\]

where

\[
\beta = \frac{(1 + 2\epsilon^2)^{2/3}}{(1 + \epsilon^2)^{1/3}}. \tag{4.4}
\]

\( \beta \) is larger for larger spectral dispersion, \( \epsilon \). The authors also found from aircraft observations
that dispersion is positively correlated with cloud droplet number concentration.

The implication of this finding is that without considering the dispersion of the cloud droplet spectrum, the effective radius may be underestimated, and hence the first indirect effect can potentially be overestimated. *Rotstayn and Liu* (2003) ran a number GCM simulations using different dispersion values obtained from empirical fitting of measurement data in *Liu and Daum* (2002), and compared these simulations to the one ran with prescribed $\beta$ values, which are constant over land and ocean. They found that by accounting for the effect of relative dispersion on effective radius in global climate model simulations, the reduction in first aerosol indirect effect ranges between 12% and 35% in terms of radiative forcing.

Furthermore, *Peng and Lohmann* (2003) showed that the comparison between modeled and observed cloud albedo during field campaigns improved when accounting for the dispersion effect on effective radius during the albedo calculations through the use of $\beta$ as given in equation (4.4). To investigate the impacts of dispersion on aerosol indirect effect, they applied $\beta$ values from field studies in GCM study using ECHAM4 and obtained a reduction of 0.2 W m$^{-2}$ in global average aerosol indirect effect.

By running parcel model with marine stratus/stratocumulus observational data as input, *Peng et al.* (2007) revealed that when aerosol number concentration increases, the width of the cloud spectra increases, however such increase diminishes when updraft velocity increases. They also examined the sensitivity of the dispersion effect on chemical composition, and found that particles containing sulfate and less soluble organics enhanced the dispersion effect. The condensation of gaseous HNO$_3$ on aerosol particles leads to increases in cloud droplet number concentration and broader spectra.

They explained the cloud droplet spectral broadening is due to slower growth rates when aerosol number concentration increases. *Yum and Hudson* (2005) suggested from cloud parcel model simulation results that the broadness of the cloud droplet spectrum depended on cloud supersaturation. The wider spectrum is found in higher concentration of cloud droplets or weaker updrafts.
On the other hand, other previous studies showed either no significant correlation or negative correlation between droplet number concentration and standard deviation. Hudson et al. (2012) concluded from 17 flights from the Rain in Cumulus over the Ocean project (RICO) that the standard deviation of the cloud droplet spectra was inversely related to the CCN concentrations. They ran a series of cloud model simulations and concluded that when updraft velocity increases, the correlation between standard deviation and CCN changes from positive to negative. Aircraft measurements of marine stratocumulus during the Second Aerosol Characterization Experiment (ACE2) however did not show much difference in standard deviation of the droplet spectra between maritime and polluted clouds (Pawlowska et al., 2006). In addition, there are 3D large-eddy simulations (Lu and Seinfeld, 2006) demonstrating that the dispersion decreases when aerosol number concentration, $N_a$, increases for $N_a < 1000 \text{ cm}^{-3}$.

Apart from parameterization of effective radius and hence evaluate the aerosol first indirect effect, spectral dispersion plays an essential role in parametrizing the autoconversion, the process at which cloud droplets transform to rain drops in cloud microphysical models Liu and Daum (2004); Liu et al. (2006); Xie et al. (2013).

The modeling studies performed to date all assume comparatively simple aerosol distributions. For example in Peng et al. (2007), log-normal size distributions of aerosol with uniform composition of sodium chloride or ammonium sulfate or a prescribed mixture of organic and sulfate are assumed in the model input. In the LES study by Lu and Seinfeld (2006), the aerosol population is assumed to be log-normally distributed in size and contains only ammonium sulfate. Liu and Daum (2002) speculated that “One explanation for the simultaneous increases in $\epsilon$ and $N$ is that anthropogenic aerosols have a more complex chemical composition and a broader size distribution than marine aerosols, ...”. With our particle-resolved model framework, we can investigate whether there is any relationship between the chemical composition complexity and the dispersion of the cloud droplet spectrum, using a library of particle-resolved cloud parcel scenarios described in Section 3.3.2 and Table 3.2 in
conjunction with a new concept of quantifying the “complexity” of a population in terms of mixing state metrics, introduced by Riemer and West (2013).

The purpose of this study is to investigate the impacts of aerosol mixing state on the dispersion of cloud droplet spectrum. The methodology is detailed in the next session. It is followed by the result section and the conclusion.

4.2 Methodology

We applied the particle-resolved model PartMC-MOSAIC (Riemer et al., 2009) to simulate the temporal evolution of the physicochemical properties of an aerosol population in an urban plume environment during a two-day period. We then performed 72 cloud parcel simulations initialized by the selected aerosol populations based on the output from the scenarios library M1 defined in Chapter 3, the details can be found in Tables 3.1 and 3.2.

To further investigate any relationship between the dispersion of a cloud droplet spectrum and the chemical composition complexity of an aerosol population, we employ the concepts of quantifying mixing state recently developed by Riemer and West (2013). Inspired by the information-theoretic entropy measures used in other disciplines such as ecology the authors introduced the average per-particle species diversity $D_\alpha$ and the bulk population diversity $D_\gamma$. Parameter $D_\alpha$ is a measure of the average effective number of chemical species in each particle, and $D_\gamma$ is the effective number of species in the population. The values of $D_\alpha$ and $D_\gamma$ range between 1 and $A$, where $A$ is the total number of species contained in a population. From these two measures, a mixing state index, $\chi$ is formulated as the ratio of $(D_\alpha - 1)/(D_\gamma - 1)$, which indicates the degree to which a population is internally mixed. When $\chi$ is 1, the population is completely internally mixed, when $\chi$ is 0, it means completely externally mixed. For the details of how to calculate the three quantities, reader are referred to Tables D.1 and D.2 in the appendix of this chapter.

Figure 4.1 illustrates the concepts of these three diversity measures in a phase space
spanned by \(D_\alpha, D_\gamma\). In Figure 4.1, there are seven example aerosol populations denoted by \(\Pi^i, i\) from 1 to 7, and they are described by unique pairs of \(D_\alpha\) and \(D_\gamma\). Any two of the three diversity measures are able to characterize a population in this phase space regarding its chemical composition diversity.

First, for \(\Pi^1\), all the particles contain only one species, meaning the whole population contains only 1 species and the average number of species contained in a particle is also 1. Thus both \(D_\alpha\) and \(D_\gamma\) are 1. For \(\Pi^3\), each particle contain only 1 species, so again \(D_\alpha\) is 1, however, since the population is composed of three species in equal proportion, \(D_\gamma\) is 3. For \(\Pi^4\), for the same reason, \(D_\alpha\) is 1, and since the population contains two species in unequal proportion, \(D_\gamma\) is less than 2. For \(\Pi^1, \Pi^3\) and \(\Pi^4\), since all the particles are pure particles, i.e. contain only one species, the population is completely external mixed, and \(\chi\) is 0 according to the definition.

Populations \(\Pi^2, \Pi^3\) and \(\Pi^5\) are located on the line of \(D_\gamma = 3\), indicating that these three populations have three aerosol species in equal bulk amounts, while their different \(D_\alpha\) values implies differences in the average per-particle species number. Each particle in \(\Pi^2\) contains three species in equal proportion, hence \(D_\alpha = 3\). Since some particles in \(\Pi^5\) contain 2 species, some contain 3 species, \(D_\alpha\) lies between 2 and 3.

Populations \(\Pi^1, \Pi^6\) and \(\Pi^2\) are all composed of identical particles, hence by definition have \(\chi = 1\) (completely internally mixed). The completely externally mixed line (\(\chi = 0\) line) and completely internally mixed line (\(\chi = 1\) line) converges at where \(\Pi^1\) is. \(\Pi^7\) is one of the many intermediate populations between completely internally mixed and externally mixed populations.

### 4.3 Results

In subsection 4.3.1, we first discuss the statistical quantities of cloud droplet size spectra from the 72 cloud parcel simulations, including standard deviation, average diameter and
Figure 4.1: Mixing state diagram illustrating the concepts of average per-particle diversity $D_\alpha$, bulk population diversity $D_\gamma$, and the mixing state parameter $\chi$. (Adapted from Riemer and West (2013))
relative spectral dispersion, which is the ratio of the two former quantities. Then we explore the correlation of the standard deviation and skewness of the cloud droplet size spectrum. Subsection 4.3.2 presents how the three diversity measures, $D_\alpha$, $D_\gamma$ and $\chi$ of various aerosol populations in scenario library M1 evolve as functions of plume time. Subsection 4.3.3 presents of the relationship between diversity measures and relative spectral dispersion of cloud droplet spectrum resulting from the 72 cloud parcel simulations.
4.3.1 Statistical quantities of cloud droplet size spectrum

In Figure 4.2(a), the standard deviations, $\sigma$, are shown as a function of cloud droplet number concentration $N_d$, and the symbols are colored according to the cooling rate, red stands for $0.15 \text{ K min}^{-1}$, green for $0.5 \text{ K min}^{-1}$ and blue $0.85 \text{ K min}^{-1}$. At a given cooling rate, standard deviations of the cloud droplet spectra and cloud droplet number concentration are positively correlated with a correlation coefficient of 0.9. This is consistent with the findings in Liu and Daum (2002); Peng and Lohmann (2003); Peng et al. (2007), which showed that larger standard deviations of droplet spectra are associated with larger $N_d$.

In Figure 4.2(b), the average diameters have an inverse relationship with the $N_d$, this is as expected from the adiabatic cloud parcel model simulations. The stronger the cooling rate, the larger is the amount of liquid water content, hence the larger is the average diameter. The relative spectral dispersion relationship with $N_d$ is shown in Figure 4.2(c). As the ratio of the standard deviation to the average diameter, dispersion is positively correlated with $N_d$ and negatively correlated to cooling rate. This is consistent with previous findings Liu and Daum (2002); Peng and Lohmann (2003); Peng et al. (2007).

In Figure 4.2(d), we show the skewness of the cloud droplet spectrum as function of $N_d$. The skewness of droplet spectra with large $N_d$ or weak cooling rate (red circles) tends to be negative. To explore the skewness of the droplet spectrum further, we plot the standard deviation versus skewness of the droplet spectrum in Figure 4.3. Most cases with weak cooling rate (red circles) have large standard deviation associated with negative skewness.

This implies that for weak cooling rates, numerous small-size cloud droplets exist, leading to a long left tail in the cloud droplet spectrum. This is caused by small per-droplet growth rates for the weak cooling rates as suggested by Peng et al. (2007). We found some cases where the small droplets evaporate, increasing the dispersion further.

For stronger cooling rates (green and blue circles), those spectra that are more symmetric (skewness close to 0) have smaller standard deviations than their counterparts with more
4.2 Overview of diversity measures of aerosol population

Liu and Daum (2002) suggested that the chemical complexity of an aerosol population may be related to the dispersion of the cloud droplet population. Here we investigate this question using the particle-resolved cloud parcel simulations in conjunction with a new concept to
We employed three quantitative measure of the chemical diversity ($D_\alpha$ and $D_\gamma$) and mixing state ($\chi$) of a population proposed by *Riemer and West* (2013) and summarized in Section 4.2 to investigate the relationship between relative spectral dispersion of a cloud droplet spectrum and (1) the chemical diversity of the cloud droplet population and (2) the extent to which the cloud droplet population is internally mixed. We calculate for each of the 72 cloud droplet populations, the values of $D_\alpha$, $D_\gamma$ and $\chi$ according to the formulae in *Riemer and West* (2013) (refer to Tables D.1 and D.2 in the Appendix to this chapter). However we perform the calculations in two different ways. For the first way, we compute the mass fractions based on the individual model species in each particle. For the second way, we first classify the aerosol chemical species into two groups according to their hygroscopicity, namely the rather hydrophobic species black carbon plus primary organic carbon and the remaining, more hygroscopic species (inorganics and secondary organics) contained in each particle. Then we calculate the mass fractions for these two grouped species. Figure 4.5 illustrates these two approaches of calculating the mass fraction of aerosol species contained in a particle. The purpose of this is to attribute the chemical diversity to hygroscopic and hydrophobic aerosol species only, irrespective of specific species contained in individual particles. We exclude the mass fraction of liquid water in order to account for the chemical
Figure 4.5: The two approaches of calculating mass fraction of calculating the mass fraction of aerosol species, the individual species-based (left) and grouped species-based (right) approach.

Figure 4.6: Plume time series of $D_{\alpha 1}$ and $D_{\alpha 2}$.

diversity due to non-water chemical species only.

We denote average particle diversity, bulk population diversity and mixing state index as $D_{\alpha 1}$, $D_{\gamma 1}$ and $\chi_1$ for the individual species-based calculation and $D_{\alpha 2}$, $D_{\gamma 2}$ and $\chi_2$ for the group species-based calculation. In the latter case, the maximum value of $D_{\alpha 2}$ and $D_{\gamma 2}$ is 2 in Figure 4.6 (right panel) and Figure 4.7 (right panel).

To illustrate the evolution of average particle diversity, bulk population diversity and mixing state index as a function of plume time, we calculate these quantities in the two ways described above for the total aerosol populations for the six environmental scenarios in M1 defined in Chapter 3. In Figure 4.6–4.8, each panel presents six curves, the magenta, sky blue and yellow stand for scenarios E100, E25, and E2.5 respectively, while the solid
From Figure 4.6, both measures of average particle diversity, $D_{\alpha_1}$ and $D_{\alpha_2}$ reveal that the average number of species contained in each particle is relatively small in early hours. This is because the population mainly contain freshly emitted particles or pure background particles. At later hours, the particles interact with each other through coagulations or with gaseous components through condensation, and as a result the number of species per particle on average increases gradually. From $t_p=12$ to $t_p=24$, $D_{\alpha_1}$ decreases slightly because there is evaporation of ammonium nitrate during night time (refer to Chapter 2 and Chapter 3); however, $D_{\alpha_2}$ does not drop during this period because ammonium nitrate is regarded as a member in grouped-species, its evaporation does not affect the number of grouped species. The evolution of $D_{\alpha}$ for the six scenarios behave differently as the interactions of the particles with the surrounding environment are different. Both bulk population diversity $D_{\gamma_1}$ and $D_{\gamma_2}$ increase in early hours, then stay in a relatively flat manner with some fluctuations (Figure 4.7). $D_{\gamma_1}$ evolution behaves similarly as $D_{\alpha_1}$. From Figure 4.8, the aerosol populations at early hours show that the particles are relatively more externally mixed as measured in both $\chi_1$ and $\chi_2$, and are gradually becoming internally mixed.
The temporal evolution of the three diversity measures is a result of complex interaction of various atmospheric processes, i.e., dilution, emission, coagulation, and condensation. As shown in Figure 4.6–Figure 4.8, different environmental scenarios shape the diversity of the populations differently because of the different interactions of the physical processes. Comparing the plume times series of the two sets of diversity measures, the individual species-based and grouped species-based, their temporal evolutions are different from each other. This difference stems from the way the species are grouped in the grouped species-based approach and how the various physical processes interplay with the relevant grouped species. The grouped species-based approach presented here is done according to hygroscopicity, along the same thought, the grouped species-based approach can be applied according to absorbing and non-absorbing aerosol species when investigating the impact of particle diversity on aerosol optical properties.

4.3.3 Diversity measures and their relationships with dispersion

To illustrate the relationship between cloud droplet spectral dispersion and diversity, we use the mixing state index and diversity measures based on the cloud droplet residuals (excluding the interstitial aerosol).

When the results shown in 4.2 (bottom left panel) are colored according to the values of
Figure 4.9: Relative spectral dispersion versus cloud droplet number concentration, colored by $D_{\alpha 1}$ (left) and $D_{\alpha 2}$ (right)

Figure 4.10: Relative spectral dispersion versus cloud droplet number concentration, colored by $D_{\gamma 1}$ (left) and $D_{\gamma 2}$ (right)

$D_\alpha$, $D_\gamma$ and $\chi$, Figure 4.9–Figure 4.11 are obtained. Both the individual species-based and grouped species-based results are presented here.

There is no obvious relationship between the relative spectral dispersion and the average particle diversity $D_{\alpha 1}$ or $D_{\alpha 2}$ or the population diversity $D_{\gamma 1}$ or $D_{\gamma 2}$ (Figure 4.9–Figure 4.10). This implies that a chemically complex population does not necessarily lead to a more diverse size distribution of cloud droplets. This contrasts with the speculation in Liu and Daum (2002) that more complex chemical composition of anthropogenic aerosols would lead to broader cloud droplet spectrum.
Figure 4.11: Relative spectral dispersion versus cloud droplet number concentration, colored by $\chi_1$ (left) and $\chi_2$ (right)

Likewise, no obvious relationship between the degree of internal mixture of a population and the spectral dispersion of the droplet population is found. As shown in both panels of Figure 4.11 (focusing on the lower left quadrant in each panel), both externally mixed and internally mixed droplet populations are possible to have similar dispersion values. On the other hand, populations with similar internal mixing state indices can have very different relative spectral dispersion values. These findings are observed in both mixing state indices, individual species-based ($\chi_1$) grouped species based ($\chi_2$). Note that in our scenarios library M1, the populations achieving high cloud droplet number concentrations are at $t_p=12$ h, and the cloud droplet residue in these population are rather internally mixed. Hence, there is no scenarios with high $N_d$ associated with low $\chi$ values.

### 4.4 Conclusion

We used the particle-resolved aerosol PartMC-MOSAIC and particle-resolved adiabatic cloud parcel model to investigate the factors affecting the spectral dispersion of the cloud droplet spectrum. Each cloud parcel model simulation is initialized by one of the 24 aerosol populations originating from six urban plume scenarios encompassing a wide range of black carbon emission rates and background aerosol number concentrations which undergo atmospheric
aging. The cloud parcel simulations are conducted for three different cooling rates to study how the cooling rate influences the dispersion of the droplet spectrum. We found that the spectral dispersion of the cloud droplet spectrum is positively correlated with cloud droplet number concentration, and negatively correlated with the cooling rate, which is consistent with previous finding by *Liu and Daum* (2002); *Peng and Lohmann* (2003); *Peng et al.* (2007).

More importantly, this study is the first time the quantitative measures of chemical diversity and mixing state index proposed by *Riemer and West* (2013) have been employed, in an attempt to shed light on any relationship between the chemical complexity and the spectral dispersion of a cloud droplet population. We found that chemically complex droplet populations of large $D_\gamma$ or $D_\alpha$ do not necessarily result larger dispersion values. Furthermore, the relative dispersion values span a range of values, regardless of the magnitude of mixing state index, $\chi$, the extent of being internally or externally mixed.

In summary, the relative dispersion principally depends on cloud droplet number concentration and cooling rate of the cloud parcel, chemical diversity and extent of being internally mixed both do not affecting spectral dispersion. The growth kinetic of the individual droplets and their mutual competition for water vapor, which do influence the broadness of the droplet spectrum, are not significantly determined by the complexity of the chemical composition and the extent of how aerosols are internal mixed.
Chapter 5
Conclusions

5.1 Overview

This dissertation focuses on the question: What is the impact of BC mixing state on cloud microphysical quantities? In answering this question, the work contributes to the following three areas. First, a particle-resolved cloud parcel model was developed. The cloud parcel model simulations were initialized by the model output from the particle-resolved aerosol model, PartMC-MOSAIC, to simulate the competition for water vapor among particles in a population. Second, a methodology was developed to quantify the errors in cloud microphysical quantities due to simplified model representations of the aerosol population. The methodology was applied to a wide range of scenarios to investigate the sensitivity of these errors to environmental conditions. Third, taking the advantage of the particle-resolved framework established by PartMC-MOSAIC and the cloud parcel model, a process-level understanding of the relationship between activation of individual CCN and their mixing state was performed.

Several important findings emerged from the error quantification framework. First, the error in activation fraction due to simplified aerosol mixing state representation ranged within ±25% for a BC-containing urban plume under a wide range of environmental scenarios investigated in this dissertation. This is consistent with the error in \( N_d \) prediction in
large scale model (Pringle et al., 2009) and CCN closure studies (Sotiropoulou et al., 2006). Second, the error in activation fraction and in BC scavenged mass fraction are not necessarily equivalent in magnitude. However, both errors are significantly larger for the aerosol populations containing both freshly emitted hydrophobic particles and hygroscopic particles than those that have been aged for a few hours (without adding fresh emissions). Third, the relative spectral dispersion of the cloud droplet spectrum is not primarily correlated with internal mixing extent of the cloud residue population; while simplified aerosol mixing state representation leads to an error range (-30%, +60%) in relative dispersion under a wide range of environments.

The main findings of the individual components of this work are summarized below, followed by a discussion of future directions at the end of this chapter.

5.2 Summary of findings

5.2.1 Cloud parcel model development

Chapter 2 presents the development of a particle-resolved cloud parcel model. The cloud parcel model is initialized by the particle-resolved output from PartMC-MOSAIC and simulates the competition for water vapor among all particles in the population as the parcel experiences cooling. In this way, the activation of CCN and the condensational growth of individual cloud droplets are simulated with the complete information of the mixing state of the aerosol particles, without any internal mixture assumptions as it is common practice in traditional aerosol models. The particle-resolved cloud parcel model capability is part of the open source code base.
5.2.2 Quantification of the importance of BC mixing state

Framework for error quantification. Using the newly-established particle-resolved cloud parcel model framework, Chapter 2 describes how to quantify the error in various cloud microphysical quantities that is introduced by assuming a simplified representation of the aerosol population. Specifically, we used this capability to quantify the relative importance of size information versus composition information for the prediction of the cloud droplet number fraction, the mass fraction of black carbon that is nucleation-scavenged, the cloud droplet effective radius, and the relative dispersion of the droplet size distribution by introducing averaging of particle-resolved information within prescribed bins. The error is quantified by comparing the cloud microphysical quantities computed from the aerosol population using the simplified representation to their counterparts using the particle-resolved reference calculation.

The error in cloud microphysical quantities are larger for populations containing both freshly emitted hydrophobic BC particles and background hydrophilic particles as an externally mixture compared to that for more internally mixed populations. For the cloud droplet number fraction, both composition averaging and size-bin averaging individually led to an error of less than 25% for all cloud parcel simulations, while averaging in both size bins and composition resulted in errors of up to 34% for the base case cooling rate of 0.5 K/min. In contrast, for the nucleation-scavenged black carbon mass fraction, the results for size-bin averaging tracked the reference case well, while composition averaging, with or without size-bin averaging, led to overestimation of this quantity by up to 600%. These findings imply that, first, the predictions of microphysical quantities suffer from a larger error for populations that are an external mixture of chemically distinct particles. Second, the magnitude of the errors depends on the specific microphysical quantities examined, and a small error in one quantity does not translate into small errors for the other quantities.
Sensitivity study of errors to environmental conditions. Chapter 3 presents a sensitivity study of the errors to environmental conditions to generalize the results described in Chapter 2. A scenario library was constructed by varying three input parameters of the urban plume scenarios, namely the BC emission rates, the background particle number concentrations, the gas emission rates, and one input parameter of the the cloud parcel simulations, namely the cooling rate.

The following patterns regarding the dependence of the errors on environmental conditions emerged: for the four microphysical quantities investigated, the largest error occurs when the aerosol populations from early plume hours are used to initialized cloud parcel simulations for all the environmental scenarios. Broadly speaking, for the nucleation-scavenged black carbon mass fraction, the error decreases for increasing cooling rates, keeping other environmental conditions the same, but this relationship is not evident for the other three microphysical quantities. Overpredictions are prevalently found in most of the scenarios for cloud droplet number fractions, BC nucleation-scavenged mass fractions, and relative spectral dispersion, while underpredictions commonly occur for effective radius. Besides, the errors for those four microphysical quantities in lower gas emission rates environments are larger than their counterparts in higher gas concentration environments.

5.2.3 Process-level analysis

Plume effect and parcel effect. Chapter 3 also offers a process-level analysis about the change in cloud droplet number concentration associated with the change in environmental conditions. Reductions in black carbon emission rates and background particle concentration cause changes in cloud droplet number concentration $N_d$. The extent of increase or decrease depends on underlying aerosol population characteristics and the cloud parcel cooling rate. A metric is developed to attribute the change in $N_d$ obtained (at the same cloud parcel cooling rate) between two environmental scenarios respectively to (1) the difference in aerosol population (called plume effect) and (2) to the difference in water vapor competition (called
A wide range of plume and parcel effect interaction patterns is found, which reflects the complex interactions of both during cloud droplet formation. Reducing the aerosol background concentration or the BC emission rate results in a reduction in $N_d$ for most scenarios, with a negative plume effect dominating a positive parcel effect. However, exceptions to this pattern are found for conditions with high aerosol loading, conditions where BC exists externally mixed amongst hygroscopic background aerosol, or conditions with low cooling rates.

**Factors that influence relative dispersion of cloud droplet spectra.** A long-standing question in the literature is what determines the relative dispersion of cloud droplet spectra. Chapter 4 presents an investigation of this question using the model results from the cloud parcel scenario library, focusing on the role of aerosol mixing state for this question. The degree of internal versus external mixture of the underlying aerosol populations was quantified using diversity measures following (Riemer and West, 2013). The results show that the relative dispersion of cloud droplet spectra is not related to the diversity of the underlying aerosol population. However, relative dispersion is strongly related to cloud droplet number concentration and cooling rate. When the cloud droplet number concentration is high or the cooling rate is weak, the supersaturation is low, resulting in smaller growth of the particles and hence broader droplet size spectrum and associated negative skewness, since droplets stay small under this conditions.

### 5.3 Discussion of future direction

**Further development of error quantification.** In this work, we evaluate the error in cloud microphysical properties due to simplified aerosol representation by averaging the particle-resolved information of the PartMC-MOSAIC model output before initializing cloud parcel model simulations. This does not take into account the effects of composition aver-
aging on the evolution of the urban plume simulation itself, which could be evaluated by running a traditional sectional model instead of PartMC-MOSAIC. It is likely that this would introduce error in the urban plume evolution, which would then contribute to additional error in the predicted cloud microphysical quantities.

**Investigation of full aerosol life cycle.** The particle-resolved model framework established in this work focused on the early stages of the cloud development, i.e. the activation process and the initial growth due to water vapor condensation. This can be further extended to gain a process-level understanding of the full aerosol life cycle. For example, by implementing collision-coalescence, the impacts of this process on aerosol composition can be studied. Further, the standard deviation of the cloud droplet spectrum has been related to entrainment as well as collision and coalescence among droplets (Hudson et al., 2012). By considering entrainment and collision and coalescence among cloud droplets in the cloud parcel model simulations, the influences of these two factors on droplet spectral dispersion and standard deviation can be studied. In addition, the particle-resolved model framework is suited to examine in-cloud chemical processing of aerosol particles since the chemical reactions depend on per-particle composition. This can be accomplished with the implementation of chemistry module in the cloud parcel model.

Extending the framework developed in this dissertation in this way, the impact of aerosol particles on clouds, and the impact of clouds on aerosol particles can be investigated.

**Investigation of importance of particle morphology.** Particle morphology may be an important factor affecting the CCN activity of aerosol particles (Sun and Ariya, 2006). Within the particle-resolved modeling framework per-particle information on shape can be stored, and then the influence of non-spherical shape and mixing state of aerosol particles on equilibrium vapor pressure as well as the error pertaining to cloud droplet number concentration due to spherical shape assumption of the particles can be investigated.
Investigation of radiative impacts of BC in cloud droplets. The radiative impacts of BC particles are determined by the particles optical properties, which are functions of per-particle composition and size, and environmental relative humidity and depend whether they are incorporated in hydrometeors or not (Jacobson, 2012). The particle-resolving model framework can be further developed to provide insight in this regard, for example, to examine the heating due to BC particles absorption and subsequent influence on CCN activities of the whole population of aerosol particles and cloud droplets. This would further the current understanding of the direct effect, the indirect effect and the semi-direct of BC aerosols.

Connections to observations. While a rigorous comparison to field observations was beyond the scope of this thesis, suitable observations are now becoming available, for example single-particle measurements which reveal particle-level physicochemical information of size and chemical composition of cloud droplet residuals. The comparison between model results and measurements should be made as long as the model inputs are constrained with the corresponding observations.
Appendix A

Appendix to Chapter 2: Cloud parcel model details

A.1 Additional model equations

For the saturation vapor pressure $P^0$ we use the expression according to Pruppacher and Klett (1997) (their Appendix to Chapter 4):

$$P^0(T) = 611 \exp \left( 17.15 \frac{T - 273.15}{T - 38} \right), \quad (A.1)$$

The corrected diffusivity coefficient for particle $i$, $D'_{v,i}$, is expressed as

$$D'_{v,i} = \frac{D_v}{1 + \frac{2D_v}{\alpha} \sqrt{\frac{2\pi M_v}{RT}} / D_i}, \quad (A.2)$$

where the diffusivity of water vapor in air is

$$D_v = \frac{0.211 \times 10^{-4}}{p/p_0} \left( \frac{T}{273} \right)^{1.94}, \quad (A.3)$$

and $\alpha$ is the thermal accommodation coefficient, which we take to be $\alpha = 1$. The variables $p$ and $p_0$ are environmental air pressure and standard surface pressure, respectively. The corrected thermal conductivity for air, $k'_{a,i}$, is given by

$$k'_{a,i} = \frac{k_a}{1 + \frac{2k_a}{\alpha \rho_{air} c_p} \sqrt{\frac{2\pi M_{air}}{RT}} / D_i}, \quad (A.4)$$
where $c_p$ is specific heat capacity of air at constant pressure, $M_{\text{air}}$ is the molecular weight of air, $\rho_{\text{air}}$ is the density of air, and $k_a$ is the thermal conductivity of air given by

$$k_a = 10^{-3} (4.39 + 0.071 T).$$  \hspace{1cm} (A.5)

A.2 Implications of assuming constant values for $\kappa$

Assuming constant $\kappa$ values throughout the cloud parcel run is a simplification since $\kappa$ actually depends on the ambient relative humidity (RH). We evaluated the impact of this simplification on our results by conducting additional cloud parcel simulations where we started from different initial RH values as suggested by Petters (2012). If the results of CDNC and nucleation-scavenged BC mass concentration were sensitive to the $\kappa$-RH dependence, we would obtain different results of these quantities for simulations with different initial RH conditions. We performed test runs with initial RH of 95%, 97% and 99% using four different initial aerosol populations ($t_p = 1, 7, 15, 36$). As seen in Figure A.1, for each initial aerosol population the resultant CDNC fractions and scavenged BC mass fractions for the three initial RH conditions are within 0.3% of each other. We conclude that the sensitivity of our results to the $\kappa$-RH dependence are very small and this effect can be neglected.

A.3 Numerical solution of cloud parcel equations

The system of equations (2.3), (2.4), and (2.7) constitute a Differential-Algebraic Equation (DAE) system. We solved this system in two layers, with a per-particle Newton loop to solve (2.3) and (2.4) for $\dot{D}_i$ as a function of $D_i$ and $S_v$, and then an Ordinary Differential Equation (ODE) solver to solve the system with the state vector $x = (S_v, D_1, \ldots, D_{N_p})$.

Rather than solving the implicit equations (2.3) and (2.4) for $\dot{D}_i$, it is also possible to use
Figure A.1: (a) Activation fraction $f_N$ for plume hours $t_p = 1, 7, 15, 36$ h using three different initial conditions for RH. The base-case cooling rate of 0.5 K/min was used. (b) The same as in (a), but for nucleation-scavenged BC fraction $f_{BC}$.

the assumption that $\delta_i \ll 1$ and use a first-order Taylor expansion of the exponential in (2.3) to obtain an explicit equation for $\dot{D}_i$ (see Equation 17.70 in Seinfeld and Pandis (1997)). In a representative test-case we found that this approximate explicit approach reduced the computational cost by about 25%, at the expense of errors of 1.9% in $S_{\text{max}}$ and 1.0% in the predicted CCN concentration. We do not expect that the use of the explicit formulation would significantly alter our numerical results.

We used the the CVODE solver (Cohen and Hindmarsh, 1996) method from SUNDIALS (SUite of Nonlinear and DIfferential/ALgebraic equation Solvers) version 2.4.0 (Hindmarsh et al., 2005), with the backward-differentiation formula (BDF) method and Newton iterations due to the stiffness of the ODE system. For efficient computation we explicitly evaluated the solution of the linear system given by the Newton matrix $M = I - \gamma J$, where $I$ is the identity, $\gamma$ is a scalar parameter, and $J$ is the Jacobian matrix for the ODE system. The Jacobian matrix is very sparse, as $\dot{D}_i$ does not directly depend on $D_j$ for $j \neq i$. We can exploit this fact to explicitly solve the linear system for $M_i$ as follows. In block form we
have

\[ M = \begin{bmatrix} A & B \\ C & D \end{bmatrix} \]  \hspace{1cm} (A.6)

\[ A = 1 - \gamma \frac{\partial \dot{S}_v}{\partial S_v} \quad \quad B_i = -\gamma \frac{\partial \dot{S}_v}{\partial D_i} \]  \hspace{1cm} (A.7)

\[ C_i = -\gamma \frac{\partial \dot{D}_i}{\partial S_v} \quad \quad D_{ii} = 1 - \gamma \frac{\partial \dot{D}_i}{\partial D_i} \]  \hspace{1cm} (A.8)

for \( i = 1, \ldots, N_p \) and where we observe that \( D \) is diagonal. The solution of the block system

\[ \begin{bmatrix} A & B \\ C & D \end{bmatrix} \begin{bmatrix} u \\ v \end{bmatrix} = \begin{bmatrix} p \\ q \end{bmatrix} \]  \hspace{1cm} (A.9)

can be written using the Schur complement as

\[ u = (A - BD^{-1}C)^{-1}(p - BD^{-1}q) \]  \hspace{1cm} (A.10)

\[ v = D^{-1}(q - Cu). \]  \hspace{1cm} (A.11)

As \( A \) is \( 1 \times 1 \) and \( D \) is diagonal, (A.10) and (A.11) can be evaluated with cost \( O(N_p) \). The number of Newton iterations required is independent of \( N_p \), so the total simulation cost of the cloud parcel model is \( O(N_p) \) (linear in the number of particles, \( N_p \)).
Appendix B

Appendix to Chapter 2: Aerosol population averaging

In the following subsections we consider a single size bin containing $N_p$ particles, with particle $i$, for $i = 1, \ldots, N_p$, containing volume $v_i^a$ of species $a$, for $a = 1, \ldots, A$. We write $v^a$ for the total volume of species $a$ in all particles within the size bin, $v_i$ for the total volume of particle $i$, and $v$ for the total volume of all particles in the size bin. These quantities are given by

\[
v^a = \sum_{i=1}^{N_p} v_i^a \quad \text{(B.1)}
\]

\[
v_i = \sum_{a=1}^{A} v_i^a \quad \text{(B.2)}
\]

\[
v = \sum_{a=1}^{A} v^a = \sum_{i=1}^{N_p} v_i = \sum_{i=1}^{N_p} \sum_{a=1}^{A} v_i^a. \quad \text{(B.3)}
\]

B.1 Composition averaging

For scenario “comp” we averaged the composition of the particles within each size bin, which retains the sizes of the individual particles but alters their compositions. The composition-averaged particles have volume $\bar{v}_i^a$ of species $a$ in particle $i$, defined by

\[
\bar{v}_i^a = \frac{v^a v_i}{v}, \quad \text{(B.4)}
\]

for $a = 1, \ldots, A$ and $i = 1, \ldots, N_p$.

This results in per-particle species ratios that are all equal and the same as the total
species ratios:

\[
\frac{\tilde{v}_i^a}{\bar{v}_i} = \frac{v^a v_i}{v} \frac{1}{v_i} = \frac{v^a}{v},
\]  
(B.5)

while the individual particle volumes are preserved:

\[
\bar{v}_i = \sum_{a=1}^{A} \tilde{v}_i^a = \sum_{a=1}^{A} \frac{v^a v_i}{v} = v_i.
\]  
(B.6)

Additionally, the total species volumes are preserved:

\[
\bar{v}^a = \sum_{i=1}^{N_p} \tilde{v}_i^a = \sum_{i=1}^{N_p} \frac{v^a v_i}{v} = v^a,
\]  
(B.7)

the total particle volume are preserved:

\[
\bar{v} = \sum_{i=1}^{N_p} \sum_{a=1}^{A} \tilde{v}_i^a = \sum_{i=1}^{N_p} v_i = v,
\]  
(B.8)

and the particle volume ratios of total volume are preserved:

\[
\frac{\bar{v}_i}{\bar{v}} = \frac{v_i}{v}.
\]  
(B.9)

### B.2 Size-bin averaging

For scenario “size” we assigned the average particle volume to all particles within each size bin. The size-bin-averaged particles have volume \( \hat{v}_i^a \) of species \( a \) in particle \( i \), defined by

\[
\hat{v}_i^a = \frac{\bar{v}_i}{v_i} \frac{v}{N_p},
\]  
(B.10)

for \( a = 1, \ldots, A \) and \( i = 1, \ldots, N_p \).
The size-bin-averaging rule gives particle volumes that are the average volume:

\[ \hat{v}_i = \sum_{a=1}^{A} \hat{v}_i^a = \sum_{a=1}^{A} \frac{v_i^a}{v_i} \frac{N_p}{v} = \frac{v}{N_p}, \]  
(B.11)

while preserving the per-particle species ratios:

\[ \frac{\hat{v}_i^a}{v_i} = \frac{\frac{v_i^a}{v_i} \frac{N_p}{v}}{v_i} = \frac{v_i^a}{v_i}. \]  
(B.12)

A consequence of size-bin averaging is that the total species volumes are not preserved:

\[ \hat{v}^a = \sum_{i=1}^{N_p} \hat{v}_i^a = \sum_{i=1}^{N_p} \frac{v_i^a}{v_i} \frac{N_p}{v} \neq v^a. \]  
(B.13)

However, the total volume is preserved:

\[ \hat{v} = \sum_{i=1}^{N_p} \sum_{a=1}^{A} \hat{v}_i^a = \sum_{i=1}^{N_p} \sum_{a=1}^{A} \frac{v_i^a}{v_i} \frac{N_p}{v} = \sum_{i=1}^{N_p} \frac{v}{N_p} = v \]  
(B.14)

and the particle volume ratios of total volume are all equal:

\[ \frac{\hat{v}_i}{\hat{v}} = \frac{v/N_p}{v} = \frac{1}{N_p}. \]  
(B.15)

Note that when size-bin averaging a collection of particles within a particular size bin, the average volume assigned to each averaged particle will in general not be the center of the size bin. This is reflected in the fact that the vertical lines in Figure 2.11 are not evenly spaced.
B.3 Both composition and size-bin averaging

For scenario “both” we averaged first composition and then size within one size bin. This gives the volume of species \( a \) in particle \( i \), \( \hat{\bar{v}}^a_i \), as

\[
\hat{\bar{v}}^a_i = \frac{\bar{v}^a_i \bar{v}}{\bar{v}^i N_p} = \frac{v^a}{N_p}.
\] (B.16)

This results in particle volumes that are equal to the average volume:

\[
\hat{\bar{v}}_i = \sum_{a=1}^{A} \hat{\bar{v}}^a_i = \sum_{a=1}^{A} \frac{v^a}{N_p} = \frac{v}{N_p}
\] (B.17)

and per-particle species ratios that are all equal and the same as the total species ratios:

\[
\frac{\hat{\bar{v}}^a_i}{\bar{v}^i} = \frac{\bar{v}^a_i}{\bar{v}^i N_p} = \frac{v^a}{v}.
\] (B.18)

In addition, the total species volumes are preserved:

\[
\hat{\bar{v}}^a = \sum_{i=1}^{N_p} \hat{\bar{v}}^a_i = \sum_{i=1}^{N_p} \frac{v^a}{N_p} = v^a
\] (B.19)

and the total volume is preserved:

\[
\hat{\bar{v}} = \sum_{i=1}^{N_p} \sum_{a=1}^{A} \hat{\bar{v}}^a_i = \sum_{i=1}^{N_p} \sum_{a=1}^{A} \frac{v^a}{N_p} = \sum_{i=1}^{N_p} \frac{v}{N_p} = v,
\] (B.20)

which results in the particle volume ratios of total volume being all equal:

\[
\frac{\hat{\bar{v}}_i}{\bar{v}} = \frac{\bar{v}^i}{\bar{v} N_p} = \frac{1}{N_p}.
\] (B.21)

Note that if both averaging techniques are performed, the order of application is significant. In general, if we compute \( \hat{\bar{v}}^a_i \) (first composition then size-bin averaging) and \( \hat{\bar{v}}^a_i \) (first
size-bin then composition averaging), the results will differ, so that \( \hat{v}_i^a \neq \bar{v}_i^a \). We choose to use composition-then-size because size-then-composition results in

\[
\bar{v}_i^a = \frac{\hat{v}^a \hat{v}_i}{\hat{v}} = \frac{\hat{v}^a}{N_p}
\]  

(B.22)

and so total species volumes are not preserved:

\[
\bar{v}^a = \sum_{i=1}^{N_p} \bar{v}_i^a = \sum_{i=1}^{N_p} \frac{\hat{v}^a}{N_p} = \hat{v}^a \neq v^a.
\]  

(B.23)
Appendix C

Appendix to Chapter 3: Supplementary figures and tables

Figure C.1: Gas concentrations of several major gaseous species for the three scenarios. Panels (a) and (b) show the concentrations for G100, (c) and (d) for G50 and (e) and (f) for G25.
<table>
<thead>
<tr>
<th>B100-E100-G100-C0.85</th>
<th>0.107</th>
<th>0.437</th>
<th>0.267</th>
<th>0.162</th>
</tr>
</thead>
<tbody>
<tr>
<td>B100-E100-G100-C0.5</td>
<td>0.108</td>
<td>0.306</td>
<td>0.220</td>
<td>0.157</td>
</tr>
<tr>
<td>B100-E100-G100-C0.15</td>
<td>0.0693</td>
<td>0.123</td>
<td>0.0923</td>
<td>0.0841</td>
</tr>
<tr>
<td>B100-E25-G100-C0.85</td>
<td>0.105</td>
<td>0.333</td>
<td>0.195</td>
<td>0.120</td>
</tr>
<tr>
<td>B100-E25-G100-C0.5</td>
<td>0.102</td>
<td>0.256</td>
<td>0.160</td>
<td>0.124</td>
</tr>
<tr>
<td>B100-E25-G100-C0.15</td>
<td>0.0655</td>
<td>0.118</td>
<td>0.0889</td>
<td>0.0789</td>
</tr>
<tr>
<td>B100-E2.5-G100-C0.85</td>
<td>0.120</td>
<td>0.224</td>
<td>0.137</td>
<td>0.117</td>
</tr>
<tr>
<td>B100-E2.5-G100-C0.5</td>
<td>0.100</td>
<td>0.192</td>
<td>0.128</td>
<td>0.106</td>
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<td>B100-E2.5-G100-C0.15</td>
<td>0.06545</td>
<td>0.107</td>
<td>0.08169</td>
<td>0.0740</td>
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<td>B100-E25-G100-C0.85</td>
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<td>0.277</td>
<td>0.149</td>
<td>0.063</td>
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<td>B100-E25-G100-C0.5</td>
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<td>0.233</td>
<td>0.126</td>
<td>0.0642</td>
</tr>
<tr>
<td>B100-E25-G100-C0.15</td>
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<td>0.112</td>
<td>0.0731</td>
<td>0.0527</td>
</tr>
<tr>
<td>B100-E25-G100-C0.85</td>
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<td>0.135</td>
<td>0.082</td>
<td>0.033</td>
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<tr>
<td>B100-E25-G100-C0.5</td>
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<td>0.0781</td>
<td>0.0319</td>
</tr>
<tr>
<td>B100-E25-G100-C0.15</td>
<td>0.0555</td>
<td>0.105</td>
<td>0.0609</td>
<td>0.0315</td>
</tr>
</tbody>
</table>

Table C.1: Values for cloud droplet number concentration, $N_d$
<table>
<thead>
<tr>
<th></th>
<th>1 h</th>
<th>12 h</th>
<th>24 h</th>
<th>48 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_{\text{BC,scav}}$ (in $\mu g \text{ cm}^{-3}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B100-E100-G100-C0.85</td>
<td>0.0404</td>
<td>1.845</td>
<td>1.297</td>
<td>0.495</td>
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<td>B100-E100-G100-C0.5</td>
<td>0.0422</td>
<td>1.771</td>
<td>1.439</td>
<td>0.519</td>
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<td>B100-E100-G100-C0.15</td>
<td>0.0439</td>
<td>1.144</td>
<td>0.819</td>
<td>0.461</td>
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<td>B100-E25-G100-C0.85</td>
<td>0.0360</td>
<td>0.536</td>
<td>0.354</td>
<td>0.131</td>
</tr>
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<td>B100-E25-G100-C0.5</td>
<td>0.0536</td>
<td>0.447</td>
<td>0.318</td>
<td>0.150</td>
</tr>
<tr>
<td>B100-E25-G100-C0.15</td>
<td>0.0372</td>
<td>0.315</td>
<td>0.212</td>
<td>0.140</td>
</tr>
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<td>B100-E2.5-G100-C0.85</td>
<td>0.0441</td>
<td>0.0907</td>
<td>0.0707</td>
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</tr>
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<td>B100-E2.5-G100-C0.5</td>
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<td>0.0879</td>
<td>0.0854</td>
<td>0.0565</td>
</tr>
<tr>
<td>B100-E2.5-G100-C0.15</td>
<td>0.0408</td>
<td>0.0794</td>
<td>0.0648</td>
<td>0.0514</td>
</tr>
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<td>B10-E100-G100-C0.85</td>
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<td>2.095</td>
<td>1.247</td>
<td>0.425</td>
</tr>
<tr>
<td>B10-E100-G100-C0.5</td>
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<td>1.842</td>
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<tr>
<td>B10-E100-G100-C0.15</td>
<td>0.0314</td>
<td>1.200</td>
<td>0.990</td>
<td>0.470</td>
</tr>
<tr>
<td>B10-E25-G100-C0.85</td>
<td>0.0269</td>
<td>0.578</td>
<td>0.409</td>
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<tr>
<td>B10-E25-G100-C0.5</td>
<td>0.0302</td>
<td>0.569</td>
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<td>B10-E25-G100-C0.15</td>
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Table C.2: Values for black carbon nucleation scavenging, $m_{\text{BC,scav}}$
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<th>12 h</th>
<th>24 h</th>
<th>48 h</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>$r_{\text{eff}}$ (in µm)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B100-E100-G100-C0.85</td>
<td>8.79</td>
<td>5.55</td>
<td>6.50</td>
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<td>B100-E100-G100-C0.5</td>
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<td>B100-E100-G100-C0.15</td>
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<td>B100-E25-G100-C0.85</td>
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<td>B100-E25-G100-C0.15</td>
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Table C.3: Values for effective radius, $r_{\text{eff}}$
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<th>$24 \text{ h}$</th>
<th>$48 \text{ h}$</th>
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<td>$\epsilon$</td>
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<td></td>
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<td>B100-E100-G100-C0.85</td>
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<tr>
<td>B100-E100-G100-C0.5</td>
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<td>0.127</td>
<td>0.0735</td>
<td>0.0488</td>
</tr>
<tr>
<td>B100-E100-G100-C0.15</td>
<td>0.127</td>
<td>0.220</td>
<td>0.172</td>
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<td>B100-E25-G100-C0.85</td>
<td>0.0152</td>
<td>0.0844</td>
<td>0.0347</td>
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<td>B100-E25-G100-C0.5</td>
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<td>B10-E100-G100-C0.15</td>
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<td>B10-E25-G100-C0.85</td>
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<td>0.127</td>
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<tr>
<td>B10-E2.5-G100-C0.85</td>
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<td>0.0265</td>
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Table C.4: Values for dispersion, $\epsilon$
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<td>$S_{\text{max}}$ (in %)</td>
<td></td>
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<tr>
<td>B100-E100-G100-C0.85</td>
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<td>B100-E100-G100-C0.5</td>
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<td>0.165</td>
<td>0.229</td>
<td>0.240</td>
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<tr>
<td>B100-E100-G100-C0.15</td>
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<td>0.105</td>
<td>0.145</td>
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<tr>
<td>B100-E25-G100-C0.85</td>
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<tr>
<td>B100-E25-G100-C0.5</td>
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<tr>
<td>B100-E25-G100-C0.15</td>
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<td>0.138</td>
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<td>B100-E2.5-G100-C0.5</td>
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<td>B100-E2.5-G100-C0.15</td>
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<td>0.146</td>
</tr>
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<td>B10-E100-G100-C0.85</td>
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<td>B10-E100-G100-C0.15</td>
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<td>0.111</td>
<td>0.168</td>
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<td>B10-E25-G100-C0.85</td>
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<td>B10-E25-G100-C0.5</td>
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<td>B10-E25-G100-C0.15</td>
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<td>0.099</td>
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<td>0.189</td>
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Table C.5: Values of maximum supersaturation ratio, $S_{\text{max}}$ (in %) attained in the 10-min cloud parcel simulations.
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<tbody>
<tr>
<td>(\Delta f_N) (in %)</td>
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<tr>
<td>B100-E100-G100-C0.85</td>
<td>+8.77</td>
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<td>B100-E100-G100-C0.5</td>
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<td>B100-E100-G100-C0.15</td>
<td>-8.69</td>
<td>+1.93</td>
<td>+11.35</td>
<td>+10.20</td>
</tr>
<tr>
<td>B100-E25-G100-C0.85</td>
<td>+11.74</td>
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<td>B100-E25-G100-C0.5</td>
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<td>+1.53</td>
<td>+7.47</td>
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<td>B100-E25-G100-C0.15</td>
<td>+2.36</td>
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<td>+1.78</td>
<td>-0.91</td>
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<td>-0.19</td>
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<td>B10-E100-G100-C0.15</td>
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</tr>
<tr>
<td>B10-E25-G100-C0.85</td>
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<td>B10-E25-G100-C0.5</td>
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<tr>
<td>B10-E25-G100-C0.15</td>
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<td>+7.12</td>
<td>-2.69</td>
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<td>B10-E2.5-G100-C0.85</td>
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<td>-0.85</td>
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B10-E100-G50-C0.85    | +9.03  | +22.32 | +15.84  | +1.55   |
B10-E100-G50-C0.5     | +16.43 | +11.53 | +14.05  | +4.78   |
B10-E100-G50-C0.15    | -12.12 | +12.98 | +13.77  | +5.86   |

B100-E100-G25-C0.85   | +15.9  | +21.98 | +15.52  | +4.17   |
B100-E100-G25-C0.5    | +35.41 | +20.65 | +22.46  | +13.46  |
B100-E100-G25-C0.15   | +10.38 | +12.17 | +14.32  | +6.82   |

Table C.6: Error in cloud droplet fraction, \(f_N\)
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<td>$\Delta m_{BC,\text{scav}}$ (in %)</td>
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<td>+58.2</td>
<td>+46.8</td>
<td>+10.2</td>
</tr>
<tr>
<td>B100-E25-G100-C0.85</td>
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<td>+26.8</td>
<td>+10.5</td>
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</tr>
<tr>
<td>B100-E25-G100-C0.5</td>
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<td>+20.3</td>
<td>+0.303</td>
</tr>
<tr>
<td>B100-E25-G100-C0.15</td>
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<td>+41.2</td>
<td>+51.9</td>
<td>+5.83</td>
</tr>
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<td>B100-E2.5-G100-C0.85</td>
<td>+28.6</td>
<td>+20.23</td>
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<td>B100-E2.5-G100-C0.5</td>
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<td>+6.00</td>
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</tr>
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<td>B10-E100-G100-C0.5</td>
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Table C.7: Error in BC nucleation-scavenged mass fraction, $f_{BC}$
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<tr>
<td>$r_{\text{eff}}$ (in %)</td>
<td></td>
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<tr>
<td>B100-E100-G100-C0.85</td>
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<td>-0.99</td>
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<tr>
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Table C.8: Error in effective radius, $r_{\text{eff}}$
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<td>+23.06</td>
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<td>+11.12</td>
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<tr>
<td>B100-E100-G100-C0.15</td>
<td>+6.23</td>
<td>+1.40</td>
<td>-1.04</td>
<td>+6.82</td>
</tr>
<tr>
<td>B100-E25-G100-C0.85</td>
<td>+27.28</td>
<td>-0.90</td>
<td>-5.33</td>
<td>+10.79</td>
</tr>
<tr>
<td>B100-E25-G100-C0.5</td>
<td>-17.30</td>
<td>+7.49</td>
<td>+29.52</td>
<td>-17.60</td>
</tr>
<tr>
<td>B100-E25-G100-C0.15</td>
<td>+6.44</td>
<td>-3.48</td>
<td>+11.39</td>
<td>-4.27</td>
</tr>
<tr>
<td>B100-E2.5-G100-C0.85</td>
<td>-0.19</td>
<td>+2.59</td>
<td>-6.90</td>
<td>-19.03</td>
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<tr>
<td>B100-E2.5-G100-C0.5</td>
<td>-3.44</td>
<td>-32.33</td>
<td>+7.27</td>
<td>-0.71</td>
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<tr>
<td>B100-E2.5-G100-C0.15</td>
<td>+8.68</td>
<td>-1.52</td>
<td>+1.32</td>
<td>-6.19</td>
</tr>
<tr>
<td>B10-E100-G100-C0.85</td>
<td>-18.27</td>
<td>-8.10</td>
<td>+16.58</td>
<td>-0.28</td>
</tr>
<tr>
<td>B10-E100-G100-C0.5</td>
<td>+44.37</td>
<td>+2.10</td>
<td>+16.24</td>
<td>+1.02</td>
</tr>
<tr>
<td>B10-E100-G100-C0.15</td>
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<td>-1.17</td>
<td>-8.88</td>
<td>-19.72</td>
</tr>
<tr>
<td>B10-E25-G100-C0.85</td>
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<td>+11.46</td>
<td>-9.94</td>
<td>-3.67</td>
</tr>
<tr>
<td>B10-E25-G100-C0.5</td>
<td>-23.11</td>
<td>+12.90</td>
<td>-8.10</td>
<td>+4.15</td>
</tr>
<tr>
<td>B10-E25-G100-C0.15</td>
<td>+17.57</td>
<td>+1.49</td>
<td>+12.05</td>
<td>-12.95</td>
</tr>
<tr>
<td>B10-E2.5-G100-C0.85</td>
<td>-1.64</td>
<td>-1.63</td>
<td>+2.23</td>
<td>-4.06</td>
</tr>
<tr>
<td>B10-E2.5-G100-C0.5</td>
<td>+10.56</td>
<td>+8.65</td>
<td>-8.94</td>
<td>+46.36</td>
</tr>
<tr>
<td>B10-E2.5-G100-C0.15</td>
<td>+5.18</td>
<td>+16.58</td>
<td>+6.13</td>
<td>+8.34</td>
</tr>
<tr>
<td>B100-E100-G50-C0.85</td>
<td>-13.75</td>
<td>+61.62</td>
<td>+15.41</td>
<td>-8.46</td>
</tr>
<tr>
<td>B100-E100-G50-C0.5</td>
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<td>+6.79</td>
<td>+36.94</td>
<td>-3.63</td>
</tr>
<tr>
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<td>+4.72</td>
<td>-0.16</td>
<td>-10.62</td>
</tr>
<tr>
<td>B100-E100-G25-C0.85</td>
<td>-12.64</td>
<td>+21.68</td>
<td>-1.24</td>
<td>+1.04</td>
</tr>
<tr>
<td>B100-E100-G25-C0.5</td>
<td>+62.31</td>
<td>+20.25</td>
<td>+30.43</td>
<td>+22.69</td>
</tr>
<tr>
<td>B100-E100-G25-C0.15</td>
<td>+25.38</td>
<td>+2.15</td>
<td>+0.31</td>
<td>-8.82</td>
</tr>
</tbody>
</table>

Table C.9: Error in dispersion, $\epsilon$
Appendix D

Appendix to Chapter 4: Supplementary tables

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_i^a$</td>
<td>mass of species $a$ in particle $i$</td>
</tr>
<tr>
<td>$\mu_i = \sum_{a=1}^{A} \mu_i^a$</td>
<td>total mass of particle $i$</td>
</tr>
<tr>
<td>$\mu^a = \sum_{i=1}^{N} \mu_i^a$</td>
<td>total mass of species $a$ in population</td>
</tr>
<tr>
<td>$\mu = \sum_{i=1}^{N} \mu_i$</td>
<td>total mass of population</td>
</tr>
<tr>
<td>$p_i^a = \frac{\mu_i^a}{\mu}$</td>
<td>mass fraction of species $a$ in particle $i$</td>
</tr>
<tr>
<td>$p_i = \frac{\mu_i}{\mu}$</td>
<td>mass fraction of particle $i$ in population</td>
</tr>
<tr>
<td>$p^a = \frac{\mu^a}{\mu}$</td>
<td>mass fraction of species $a$ in population</td>
</tr>
</tbody>
</table>

Table D.1: Aerosol mass and mass fraction definitions and notations. The number of particles in the population is $N$, and the number of species is $A$. (Adapted from Riemer and West (2013).)
<table>
<thead>
<tr>
<th>Quantity</th>
<th>Name</th>
<th>Units</th>
<th>Range</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_i = \sum_{a=1}^{A} -p_a^i \ln p_a^i$</td>
<td>mixing entropy of particle $i$</td>
<td>—</td>
<td>0 to ln $A$</td>
<td>Shannon entropy of species distribution within particle $i$</td>
</tr>
<tr>
<td>$H_\alpha = \sum_{i=1}^{N} p_i H_i$</td>
<td>average particle mixing entropy</td>
<td>—</td>
<td>0 to ln $A$</td>
<td>average Shannon entropy per particle</td>
</tr>
<tr>
<td>$H_\gamma = \sum_{a=1}^{A} -p^a \ln p^a$</td>
<td>population bulk mixing entropy</td>
<td>—</td>
<td>0 to ln $A$</td>
<td>Shannon entropy of species distribution within population</td>
</tr>
<tr>
<td>$D_i = e^{H_i} = \prod_{a=1}^{A} (p_a^i)^{-p_a^i}$</td>
<td>particle diversity of particle $i$</td>
<td>effective species</td>
<td>1 to $A$</td>
<td>effective number of species in particle $i$</td>
</tr>
<tr>
<td>$D_\alpha = e^{H_\alpha} = \prod_{i=1}^{N} (D_i)^{p_i}$</td>
<td>average particle (alpha) species diversity</td>
<td>effective species</td>
<td>1 to $A$</td>
<td>average effective number of species in each particle</td>
</tr>
<tr>
<td>$D_\gamma = e^{H_\gamma} = \prod_{a=1}^{A} (p^a)^{-p^a}$</td>
<td>bulk population (gamma) species diversity</td>
<td>effective species</td>
<td>1 to $A$</td>
<td>effective number of species in the population</td>
</tr>
<tr>
<td>$D_\beta = \frac{D_\gamma}{D_\alpha}$</td>
<td>inter-particle (beta) diversity</td>
<td>—</td>
<td>1 to $A$</td>
<td>amount of population species diversity due to inter-particle diversity</td>
</tr>
<tr>
<td>$\chi = \frac{D_\alpha - 1}{D_\gamma - 1}$</td>
<td>mixing state index</td>
<td>—</td>
<td>0 to 100%</td>
<td>degree to which population is externally mixed ($\chi = 0$) versus internally mixed ($\chi = 100%$)</td>
</tr>
</tbody>
</table>

Table D.2: Definitions of aerosol mixing entropies, particle diversities, and mixing state index. In these definitions we take $0 \ln 0 = 0$ and $0^0 = 1$. (Adapted from Riemer and West (2013).)
Appendix E

Cloud parcel model equations

This appendix lists the equations that are implemented to form the cloud parcel code. The
variables are explained in Appendix F.

\[ P^0(T) = 611.2 \exp \left( 7.45 \ln(10) \frac{T - 273.15}{T - 38} \right) \] (E.1)

\[ \frac{\partial P^0}{\partial T}(T) = P^0(T)7.45 \ln(10) \frac{273.15 - 38}{(T - 38)^2} \] (E.2)

\[ \rho_{\text{air}} = \frac{M_{\text{air}}}{pRT} \] (E.3)

\[ U(T) = \frac{\Delta H_v \rho_w}{4T} \] (E.4)

\[ V(T) = \frac{4M_wP^0(T)}{\rho_wRT} \] (E.5)

\[ \frac{\partial V}{\partial T}(T) = \left( \frac{1}{P^0(T)} \frac{\partial P^0}{\partial T}(T) - \frac{1}{T} \right)V(T) \] (E.6)

\[ W(T) = \frac{\Delta H_v M_w}{RT} \] (E.7)

\[ X(T) = \frac{4M_w \sigma_w}{RT \rho_w} \] (E.8)

\[ Y(T) = \frac{2k_a}{\alpha \rho_{\text{air}} c_p} \sqrt{\frac{2\pi M_{\text{air}}}{RT}} \] (E.9)

\[ Z(T) = \frac{2D_v}{\alpha} \sqrt{\frac{2\pi M_{\text{w}}}{RT}} \] (E.10)

\[ V_{\text{comp}}(T) = \frac{T}{T_0} V_{\text{comp},0} \quad V_{\text{comp},0} \text{ is the computational volume at temperature } T_0 \] (E.11)

\[ \frac{\partial V_{\text{comp}}}{\partial T}(T) = \frac{V_{\text{comp},0}}{T_0} \] (E.12)
\[
\kappa_a = \frac{V_{\text{comp}}}{T} \quad \text{(E.13)}
\]

\[
k_a = 10^{-3}(4.39 + 0.071T) \quad \text{(E.14)}
\]

\[
k_a'(D_i) = \frac{k_a}{1 + Y/D_i} \quad \text{(E.15)}
\]

\[
\frac{\partial k_a'}{\partial D_i}(D_i) = \frac{k_a Y}{(D_i + Y)^2} \quad \text{(E.16)}
\]

\[
D_v = \frac{0.211 \cdot 10^{-4}}{p/p_0} \left( \frac{T}{273} \right)^{1.94} \quad \text{(E.17)}
\]

\[
D_v'(D_i) = \frac{D_v}{1 + Z/D_i} \quad \text{(E.18)}
\]

\[
\frac{\partial D_v'}{\partial D_i}(D_i) = \frac{D_v Z}{(D_i + Z)^2} \quad \text{(E.19)}
\]

\[
\kappa^a = \frac{M_w \rho_a}{M_a \rho_w} \quad \text{assuming number of ions per dissociation is 1.} \quad \text{(E.20)}
\]

\[
\kappa_i = \sum_a \kappa^a \frac{V_{a,\text{dry}}}{V_{\text{dry}}} \quad \text{(E.21)}
\]

\[
a_{wi}(D_i) = \frac{D_i^3 - D_{i,\text{dry}}^3}{D_i^3 + (\kappa_i - 1)D_{i,\text{dry}}^3} \quad \text{(E.22)}
\]

\[
\frac{\partial a_{wi}}{\partial D_i}(D_i) = \frac{3D_i^2 \kappa_i D_{i,\text{dry}}^3}{(D_i^3 + (\kappa_i - 1)D_{i,\text{dry}}^3)^2} \quad \text{(E.23)}
\]

\[
h_i(\delta, D_i, H) = k_a'(D_i)\delta - UV D_v'(D_i) \left( H - \left( \frac{1}{1 + \delta} \right) a_{wi}(D_i) \right) \times \exp \left( W \frac{\delta}{1 + \delta} + X \frac{1}{D_i 1 + \delta} \right) \quad \text{(E.24)}
\]

\[
\frac{\partial h_i}{\partial \delta}(\delta, D_i, H) = k_a'(D_i) - \frac{UV D_v'(D_i) a_{wi}(D_i)}{(1 + \delta)^2} \left( 1 - W \frac{1}{1 + \delta} + X \frac{1}{D_i 1 + \delta} \right) \times \exp \left( W \frac{\delta}{1 + \delta} + X \frac{1}{D_i 1 + \delta} \right) \quad \text{(E.25)}
\]
\[ \frac{\partial h_i}{\partial D_i}(\delta, D_i, H) = \frac{\partial k_i^a}{\partial D_i}(D_i) \delta - UV \frac{\partial D^\prime_i}{\partial D_i}(D_i) H \]
\[ + UV \left( a_{wi}(D_i) \frac{\partial D^\prime_i}{\partial D_i}(D_i) + D^\prime_i(D_i) \frac{\partial a_{wi}}{\partial D_i}(D_i) \right) \]
\[ - D^\prime_i(D_i) a_{wi}(D_i) \frac{X}{D_i^2} \frac{1}{1 + \delta} \]
\[ \times \left( \frac{1}{1 + \delta} \right) \exp \left( W \frac{\delta}{1 + \delta} + \frac{X}{D_i} \frac{1}{1 + \delta} \right) \]  
(E.26)

\[ \frac{\partial h_i}{\partial H}(\delta, D_i, H) = -UV D^\prime_i(D_i) \]  
(E.27)

\[ 0 = h_i(\delta^*_i(D_i), D_i, H) \]  
(E.28)

\[ 0 = \frac{d}{dD_i} h_i(\delta^*_i(D_i), D_i, H) = \frac{\partial h_i}{\partial \delta}(\delta^*_i(D_i), D_i, H) \frac{\partial \delta^*_i}{\partial D_i}(D_i, H) \]
\[ + \frac{\partial h_i}{\partial D_i}(\delta^*_i(D_i), D_i, H) \]  
(E.29)

\[ 0 = \frac{d}{dH} h_i(\delta^*_i(D_i), D_i, H) = \frac{\partial h_i}{\partial \delta}(\delta^*_i(D_i), D_i, H) \frac{\partial \delta^*_i}{\partial H}(D_i, H) \]
\[ + \frac{\partial h_i}{\partial H}(\delta^*_i(D_i), D_i, H) \]  
(E.30)

\[ \frac{\partial \delta^*_i}{\partial D_i}(D_i, H) = -\frac{\partial h_i}{\partial D_i}(\delta^*_i(D_i), D_i, H) \]  
(E.31)

\[ \frac{\partial \delta^*_i}{\partial H}(D_i, H) = -\frac{\partial h_i}{\partial H}(\delta^*_i(D_i), D_i, H) \]  
(E.32)

\[ \dot{D}_i(D_i, H) = \frac{k_i^l(D_i) \delta^*_i(D_i, H)}{UD_i} \]  
(E.33)

\[ \frac{\partial \dot{D}_i}{\partial D_i}(D_i, H) = \frac{1}{UD_i} \frac{\partial k_i^l}{\partial D_i}(D_i) \delta^*_i(D_i, H) + \frac{1}{UD_i} k_i^l(D_i) \frac{\partial \delta^*_i}{\partial D_i}(D_i, H) \]
\[ - \frac{1}{UD_i} k_i^l(D_i) \delta^*_i(D_i, H) \]  
(E.34)

\[ \frac{\partial \dot{D}_i}{\partial H}(D_i, H) = \frac{k_i^l(D_i) \partial \delta^*_i}{UD_i \partial H}(D_i, H) \]  
(E.35)

\[ \dot{H}_i(D_i, H) = -\frac{2\pi}{V(T) V_{\text{comp}}(T)} \frac{D_i^{\prime 2}}{D_i} \dot{D}_i(D_i, H) \]  
(E.36)

\[ \frac{\partial \dot{H}_i}{\partial D_i}(D_i, H) = -\frac{2\pi}{V(T) V_{\text{comp}}(T)} \left( 2D_i \dot{D}_i(D_i, H) + D_i^2 \frac{\partial \dot{D}_i}{\partial D_i}(D_i, H) \right) \]  
(E.37)

\[ \frac{\partial \dot{H}_i}{\partial H}(D_i, H) = -\frac{2\pi}{V(T) V_{\text{comp}}(T)} D_i^2 \frac{\partial \dot{D}_i}{\partial H}(D_i, H) \]  
(E.38)
\[
\dot{H}_{\text{env}}(D_1, \ldots, D_N, H) = -\frac{1}{V(T)} \frac{\partial V}{\partial T}(T) \dot{T}H - \frac{1}{V_{\text{comp}}(T)} \frac{\partial V_{\text{comp}}}{\partial T}(T) \dot{T}H 
\]

\[
\frac{\partial \dot{H}_{\text{env}}}{\partial D_i}(D_1, \ldots, D_N, H) = 0
\]

\[
\frac{\partial \dot{H}_{\text{env}}}{\partial H}(D_1, \ldots, D_N, H) = -\frac{1}{V(T)} \frac{\partial V}{\partial T}(T) \dot{T} - \frac{1}{V_{\text{comp}}(T)} \frac{\partial V_{\text{comp}}}{\partial T}(T) \dot{T}
\]

\[
H = \frac{4m_w}{\rho_w V(T) V_{\text{comp}}(T)}
\]

\[
\dot{H}(D_1, \ldots, D_N, H) = \sum_{i=1}^{N} \dot{H}_i(D_i, H) + \dot{H}_{\text{env}}(D_1, \ldots, D_N, H)
\]

\[
\frac{\partial \dot{H}}{\partial D_i}(D_1, \ldots, D_N, H) = \frac{\partial \dot{H}_i}{\partial D_i}(D_i, H) + \frac{\partial \dot{H}_{\text{env}}}{\partial D_i}(D_1, \ldots, D_N, H)
\]

\[
\frac{\partial \dot{H}}{\partial H}(D_1, \ldots, D_N, H) = \sum_{i=1}^{N} \frac{\partial \dot{H}_i}{\partial H}(D_i, H) + \frac{\partial \dot{H}_{\text{env}}}{\partial H}(D_1, \ldots, D_N, H)
\]

If \(D_i < D_{i,\text{dry}}\) then we take

\[
h_i(\delta, D_i, H) = k'_a(D_{i,\text{dry}}) \delta - UV D'_v(D_{i,\text{dry}}) H
\]

\[
\frac{\partial h_i}{\partial \delta}(\delta, D_i, H) = k'_a(D_{i,\text{dry}})
\]

\[
\frac{\partial h_i}{\partial D_i}(\delta, D_i, H) = 0
\]

\[
\frac{\partial h_i}{\partial H}(\delta, D_i, H) = -UV D'_v(D_{i,\text{dry}})
\]

\[
\dot{h}_i^*(D_i, H) = \frac{UV D'_v(D_{i,\text{dry}}) H}{k'_a(D_{i,\text{dry}})}
\]

\[
\frac{\partial \dot{h}_i^*}{\partial D_i}(D_i, H) = 0
\]

\[
\frac{\partial \dot{h}_i^*}{\partial H}(D_i, H) = \frac{UV D'_v(D_{i,\text{dry}})}{k'_a(D_{i,\text{dry}})}
\]

\[
\dot{D}_i(D_i, H) = \frac{k'_a(D_{i,\text{dry}}) \delta_i^*(D_i, H)}{UD_{i,\text{dry}}}
\]

\[
\frac{\partial \dot{D}_i}{\partial D_i}(D_i, H) = 0
\]

\[
\frac{\partial \dot{D}_i}{\partial H}(D_i, H) = \frac{k'_a(D_{i,\text{dry}})}{UD_{i,\text{dry}}} \frac{\partial \delta_i^*}{\partial H}(D_i, H)
\]

\[
\dot{H}_i(D_i, H) = -\frac{2\pi}{V(T)V_{\text{comp}}(T)} D_{i,\text{dry}}^2 \dot{D}_i(D_i, H)
\]
\[
\frac{\partial \dot{H}_i}{\partial D_i}(D_i, H) = -\frac{2\pi}{V(T)V_{\text{comp}}(T)} \frac{D_{i,dry}^2}{D_i} \frac{\partial \dot{D}_i}{\partial D_i}(D_i, H) \hspace{1cm} (E.57)
\]
\[
\frac{\partial \dot{H}_i}{\partial H}(D_i, H) = -\frac{2\pi}{V(T)V_{\text{comp}}(T)} \frac{D_{i,dry}^2}{D_i} \frac{\partial \dot{D}_i}{\partial H}(D_i, H) \hspace{1cm} (E.58)
\]

For equilibriation:

\[
g_i(D_i, H) = h_i(0, D_i, H) \hspace{1cm} (E.59)
\]
\[
= H - a_{wi}(D_i) \exp \left( \frac{X}{D_i} \right) \hspace{1cm} (E.60)
\]
\[
\frac{\partial g_i}{\partial D_i}(D_i, H) = -\frac{\partial a_{wi}}{\partial D_i}(D_i) \exp \left( \frac{X}{D_i} \right) + a_{wi}(D_i) \exp \left( \frac{X}{D_i} \right) \frac{X}{D_i^2} \hspace{1cm} (E.61)
\]
Appendix F

List of variables

This appendix provides the explanation of the variables used in Appendix E.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Numerical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>thermal accommodation coefficient</td>
<td>1.0</td>
</tr>
<tr>
<td>$M_{air}$</td>
<td>molecular weight of air</td>
<td>$2.89644 \times 10^{-2}$ kg mol$^{-1}$</td>
</tr>
<tr>
<td>$M_w$</td>
<td>molecular weight of water</td>
<td>$18 \times 10^{-3}$ kg mol$^{-1}$</td>
</tr>
<tr>
<td>$M_i$</td>
<td>molecular weight of aerosol species $i$</td>
<td>species dependent</td>
</tr>
<tr>
<td>$c_p$</td>
<td>specific heat capacity of air at constant pressure</td>
<td>1004 J kg$^{-1}$</td>
</tr>
<tr>
<td>$\rho_w$</td>
<td>density of water</td>
<td>$1 \times 10^3$ kg m$^{-3}$</td>
</tr>
<tr>
<td>$\rho_i$</td>
<td>aerosol density</td>
<td>species dependent</td>
</tr>
<tr>
<td>$\kappa_i$</td>
<td>hygroscopicity of component $i$</td>
<td>species dependent</td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant</td>
<td>8.314 J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$\sigma_w$</td>
<td>surface tension (or surface energy) of water</td>
<td>0.073 J m$^{-2}$</td>
</tr>
<tr>
<td>$\Delta H_v$</td>
<td>latent heat of vaporization of water</td>
<td>$2.272 \times 10^6$ J kg$^{-1}$</td>
</tr>
<tr>
<td>$p_0$</td>
<td>standard surface pressure</td>
<td>101300 Pa</td>
</tr>
<tr>
<td>$p$</td>
<td>environmental air pressure</td>
<td>input (Pa)</td>
</tr>
<tr>
<td>$T$</td>
<td>environmental temperature</td>
<td>input (K)</td>
</tr>
<tr>
<td>$D_{dry}$</td>
<td>dry diameter of the aerosol particle</td>
<td>input (m)</td>
</tr>
<tr>
<td>$V_{dry}$</td>
<td>dry volume of the aerosol particle</td>
<td>input (m$^3$)</td>
</tr>
<tr>
<td>$V_{a dry}$</td>
<td>dry volume of species $a$ of the aerosol particle</td>
<td>input (m$^3$)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Meaning</td>
<td>Numerical value</td>
</tr>
<tr>
<td>----------</td>
<td>----------------------------------------</td>
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<td>computational volume</td>
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<tr>
<td>$D_v$</td>
<td>diffusivity coefficient</td>
<td>function (m$^2$ s$^{-1}$)</td>
</tr>
<tr>
<td>$D'_v$</td>
<td>corrected diffusivity coefficient</td>
<td>function (m$^2$ s$^{-1}$)</td>
</tr>
<tr>
<td>$\delta^*$</td>
<td>growth parameter</td>
<td>function</td>
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<tr>
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<td>water activity</td>
<td>function</td>
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<tr>
<td>$\kappa$</td>
<td>overall hygroscopicity</td>
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<tr>
<td>$\rho_{\text{air}}$</td>
<td>air density</td>
<td>function</td>
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<tr>
<td>$k_a$</td>
<td>thermal conductivity of air</td>
<td>function (J m$^{-1}$ s$^{-1}$ K$^{-1}$)</td>
</tr>
<tr>
<td>$k'_a$</td>
<td>corrected thermal conductivity of air</td>
<td>function (J m$^{-1}$ s$^{-1}$ K$^{-1}$)</td>
</tr>
<tr>
<td>$P^0$</td>
<td>saturation vapor pressure</td>
<td>function (Pa)</td>
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<td>$D_i$</td>
<td>droplet wet diameter</td>
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<tr>
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<td>mass of water vapor</td>
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</tr>
<tr>
<td>$m_i$</td>
<td>total mass of particle</td>
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<tr>
<td>$H$</td>
<td>environmental relative humidity</td>
<td>dynamical variable</td>
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<tr>
<td>$\dot{H}_i$</td>
<td>relative humidity change due to particle $i$</td>
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</tr>
<tr>
<td>$\dot{H}_{\text{env}}$</td>
<td>relative humidity change due to environment</td>
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Appendix G

PartMC-MOSAIC equations

This appendix gives a brief overview of the governing equations that form the basis for PartMC-MOSAIC. In PartMC-MOSAIC, the mass of each species contained in every particle is tracked during the period of simulation. In mathematical notation, suppose a particle population Π contains \( N_p \) particles, then we can write \( \Pi = (\vec{\mu}_1, \vec{\mu}_2, \ldots, \vec{\mu}_{N_p}) \), and each particle \( i \) is represented as a vector, \( \vec{\mu}_i = (\mu^1_i, \mu^2_i, \ldots, \mu^A_i) \in \mathbb{R}^A \), where it contains \( A \) species. \( \mu^a_i \) is the volume of species \( a \) in particle \( i \), for \( a = 1, \ldots, A \) and \( i = 1, \ldots, N_p \). It is readily to express the aerosol number concentration distribution at time \( t \), \( n(\vec{\mu}, t) \) as

\[
n(\vec{\mu}, t) = \frac{\partial^A N(\vec{\mu}, t)}{\partial \mu_1 \partial \mu_2 \ldots \partial \mu_A},
\]

where \( N(\vec{\mu}, t) \) is the cumulative aerosol number distribution at time \( t \).

PartMC-MOSAIC solves the following equation system which is a coupled pair of equations, one for a multidimensional aerosol distribution and one for concentration of gas phase, to account for various physical processes as indicated by the braces under the corresponding terms in the following equations,
\[
\frac{\partial n(\mu, t)}{\partial t} = \frac{1}{2} \int_0^{\mu_1} \int_0^{\mu_2} \ldots \int_0^{\mu_A} K(\mu', \mu - \mu') n(\mu', t) n(\mu - \mu', t) \, d\mu_1' \, d\mu_2' \ldots d\mu_A'
\]

coagulation gain

\[
- \int_0^\infty \int_0^\infty \ldots \int_0^\infty K(\mu', \mu') n(\mu', t) n(\mu, t) \, d\mu_1' \, d\mu_2' \ldots d\mu_A' + \dot{n}_{\text{emit}}(\mu, t) + \lambda_{\text{dil}}(t)n_{\text{back}}(\mu, t)
\]

coagulation loss

\[
\sum_{i=1}^C \frac{\partial}{\partial \mu_i} (c_i I_i(\mu, \bar{\mu}, t)) n(\mu, t) - \frac{\partial}{\partial \mu_{C+1}} (c_w I_w(\mu, \bar{g}, t)) n(\mu, t) + \frac{1}{\rho_{\text{dry}}(t)} \frac{d\rho_{\text{dry}}(t)}{dt} n(\mu, t)
\]

gas – particle transfer

\[
\frac{dg_i(t)}{dt} = \dot{g}_{\text{emit},i}(t) + \lambda_{\text{dil}}(t)(g_{\text{back},i}(t) - g_i(t)) + R_i(\bar{g}) + \frac{1}{\rho_{\text{dry}}(t)} \frac{d\rho_{\text{dry}}(t)}{dt} g_i(t)
\]

emission dilution chemical reaction air density change

\[
- \int_0^\infty \int_0^\infty \ldots \int_0^\infty I_i(\mu, \bar{g}, t) n(\mu, t) \, d\mu_1 \, d\mu_2 \ldots d\mu_A.
\]

gas – particle transfer

(G.2)

\[
\frac{dg_i(t)}{dt} = \dot{g}_{\text{emit},i}(t) + \lambda_{\text{dil}}(t)(g_{\text{back},i}(t) - g_i(t)) + R_i(\bar{g}) + \frac{1}{\rho_{\text{dry}}(t)} \frac{d\rho_{\text{dry}}(t)}{dt} g_i(t)
\]

emission dilution chemical reaction air density change

(G.3)

The particle population \( \Pi = (\mu_1, \mu_2, \ldots, \mu_N) \) in a Lagrangian parcel of computational volume \( V \) is stored and tracked during the simulation. This Lagrangian parcel of air is regarded as a representative sample of a well-mixed atmospheric boundary layer.

Recently, PartMC-MOSAIC is updated with the employment of weighted flow algorithm to improved efficiency. The updated PartMC-MOSAIC has been applied to an urban plume
scenarios to simulate a particle population evolution. The detailed formulation such algorithm can be found in DeVille et al. (2011).

MOSAIC is an atmospheric chemistry model developed by Zaveri et al. (2008). It simulates atmospheric chemical reactions of gas phase, intra-particle phase equilibrium, gas-particle thermodynamic equilibrium in deterministic manner. The details about MOSAIC can be found in Zaveri et al. (2008).
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