INVERSE MODELING OF CLOUD - AEROSOL INTERACTIONS

Daniel Partridge

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Cover image: Stratocumulus clouds from above – Tampere to Stockholm December 2010.
Photo by Daniel Partridge

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Who has the wisdom to count the clouds?
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1. Introduction

This thesis considers one of the first applications of inverse modeling in cloud – aerosol interactions for liquid phase clouds. In order to frame and provide context for the discussion of the results and conclusions drawn in this thesis, a brief overview of clouds aerosols, and their role in the Earth's climate system will first be given. This is followed by background information on the aerosol lifecycle and the interaction between aerosols and clouds.

1.1 Clouds, aerosols and climate

Clouds are important features of the climate system. When seen from space they exhibit a continually fluctuating pattern which on average covers about half of the Earth's surface. Clouds are a key part of the atmospheric energy budget and the hydrological cycle. In combination with atmospheric gases and aerosols, clouds alter the upwelling and downwelling radiative fluxes from the sun and the Earth through reflection, absorption and scattering. On average, clouds enforce a net cooling of the Earth's surface by reflecting a fraction of the total incoming shortwave radiation from the sun back to space. Their ability to strongly absorb in the thermal infra-red wavelengths means that clouds can also contribute to a warming of the surface by absorbing some of the upwelling longwave radiation and re-emitting a portion of this back to the surface.

Being the most visible manifestations of atmospheric water vapour, clouds have captivated scientists for many years. Luke Howard (1772-1864), a pioneer in cloud classification stated that "clouds are subject to certain distinct modifications, produced by the general causes which affect all the variations of the atmosphere; they are commonly as good visible indicators of the operation of these causes as is the countenance of the state of a person's mind or body." (Howard, 1804). Early scientists astutely realised that our ability to forecast the weather relies heavily on our ability to understand the sensitivity of clouds with respect to their environment. As Lamarck noted in 1802, "it is clear that clouds have certain general forms which are not all dependent on chance but on a state of affairs which it would be useful to recognise and determine." (Lamarck, 1802).

Thus, cloud classification highlighted the infinite variety of shapes but limited number of forms corresponding to the different balance of physical processes in the atmosphere which are responsible for the formation and evolution of clouds. Since Howard introduced his classification scheme, meteorologists have strived to measure the properties of clouds, and how they impact the weather. Clouds form when an air mass becomes supersaturated with respect to liquid water or ice. The principle mechanism by which supersaturation is reached is via the ascent of air, resulting in its adiabatic expansion and cooling to its dew-point temperature. The various types of ascent in the atmosphere give rise to the distinctively different cloud forms classified by Howard. For example, convective clouds (e.g. cumulus) are produced by the local ascent of warm buoyant air parcels in a conditionally unstable environment. The forced lifting of air as it passes over hills or mountains produces orographic clouds, whereas forced lifting of stable air produces layered or stratiform clouds.

Once the air has reached its dew-point temperature, a pre-requisite for the formation of cloud droplets is the existence of a condensation nucleus in the atmosphere for the water to condense onto. These cloud condensation nuclei (CCN) are made up of aerosols, microscopic liquid droplets or solid particles suspended in the Earth's atmosphere, representing a vital component of the atmospheric system. The first basic experiments and observations concerning the role of fine airborne particles that lead to the conclusions that atmospheric aerosols act as CCN were conducted by Coulier (1875a, b) and Aitken (1880). Aitken (1880) stated that: "Dust is the germ of which fogs and clouds are the developed phenomena. If there were no dust, there would be no fogs, no clouds, no mists, and probably no rain". Thus, particles so small that they are barely visible in the microscope strongly influence the formation of cloud systems so large that they can only be viewed in their entirety from space.

Whereas greenhouse gases have a net warming affect on the climate, atmospheric aerosols globally have a net cooling effect (IPCC, 2007). The first documented observations of the climatic effects of aerosol particles on our climate can be traced back to volcanic eruptions, such as the 1815 explosion of Mount Tambora, which by injecting large quantities of volcanic dust into the Earth's atmosphere measurably reduced sunlight reaching the surface around the world. The associated reduction in Northern Hemisphere mean temperatures (Stothers, 1984) resulted in 1816 being coined "the year without a summer". Aside from natural sources of aerosols, human activities also result in significant anthropogenic emissions of aerosols which have substantially increased the global mean aerosol burden compared to pre-industrial times (Lohmann et al., 2007). Accordingly, the emission of aerosols may be having dramatic impacts on global climate change (Charlson et al., 1992) as aerosol particles can affect the climate system via several mechanisms. Firstly, they interact directly with radiation (the direct effect) by scattering

and absorbing solar radiation. Secondly, aerosols capable of absorbing shortwave radiation, such as soot, can cause a heating of clouds and the environment within which clouds form. This may reduce cloud cover and liquid water content (the semi-direct effect) (Hansen et al., 1997). Finally, aerosols influence the radiative budget of the atmosphere by altering microphysical and radiative properties of clouds (the indirect effect).

It was not shown until the studies of Squires in 1956, in a series of pioneering measurements that the development and properties of clouds depend on the atmospheric aerosol, and not just the dynamic and thermodynamic properties of the atmosphere (meteorology). Soon after, Twomey (1959) recognized that aerosol perturbations can affect cloud properties; by showing that cloud reflectance is partially dependent on droplet size, which in turn is linked to the concentration of CCN. The net effect of an increase in CCN is to increase cloud albedo (at fixed cloud liquid water path), generally resulting in radiative cooling of the surface. This is termed the first indirect aerosol effect. The presence of more CCN can also potentially increase cloud lifetime since many small droplets deplete available water vapour such that precipitation size droplets cannot form. This feedback is termed the second indirect aerosol effect (Albrecht, 1989).

It is now widely accepted that changes in cloud albedo and lifetime associated with changes in the atmospheric aerosol may counteract to some degree the warming caused by increases in well-mixed greenhouse gases (CO_2, CH_4, N_2O, HCFCs etc). Whilst future aerosol concentrations are expected to decrease due to policies introduced in order to abate the harmful effects from aerosol particles on human health, CO_2 concentrations are projected to rise further. To what extent the aerosol direct and indirect effect masks greenhouse warming is highly uncertain (Figure 1), making it a high research priority.

The various pathways by which aerosols can affect clouds represent one of the largest uncertainties in our understanding of climate change (Kaufman et al., 2005). This uncertainty represents the inadequacy of existing frameworks and methodologies to understand the underlying processes governing cloud-aerosol interactions.

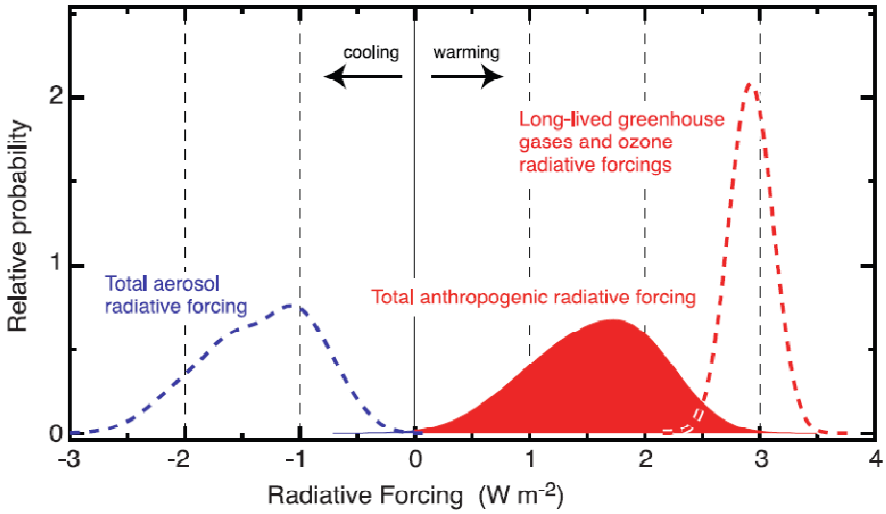

Figure 1: Probability distribution functions (PDFs) from combining anthropogenic radiative forcings derived from a one-million point Monte Carlo simulation (Boucher and Haywood, 2001). The dashed blue curve contains contributions from aerosol direct and cloud albedo radiative forcings only. Surface albedo, contrails and stratospheric water vapour radiative forcings are included in the total curve but not in the others. The height of the curve gives the relative probability of the associated value: From IPCC, 2007.

1.2 The lifecycle of atmospheric aerosols and their role in cloud formation

Aerosol particles are ubiquitous in the Earth's atmosphere. Aerosols may be solid, liquid or a mixture of both (Warneck, 1988). Their chemical composition can be highly varied, and the numerous different compounds that may be found in the particle phase of the aerosol can originate from a wide variety of natural and anthropogenic sources.

The mixing state is an important parameter that characterizes atmospheric aerosols. An external aerosol mixture is one where there is no mixing between particles of different chemical components, that is, each individual particle comprises a single chemical species. Thus, for externally mixed aerosols, the particles of the different aerosol types (e.g. sulphate and BC), are entirely physically separate. An internal aerosol mixture on the other hand is one where there is complete mixing between particles of different

chemical components so that all aerosol particles of a given size have the same chemical composition.

The diverse morphology and composition of aerosols reflects their origin and ageing (chemical and physical processing) in the atmosphere. According to the formation mechanism, atmospheric aerosols can be divided into two groups: primary and secondary atmospheric aerosols.

Primary, mechanically generated, atmospheric aerosols are emitted directly into the atmosphere. Examples of these include emissions of sea-salt, volcanic dust, smoke and soot, re-suspension of windblown dust or minerals from deserts, and organics such as pollen and spores. Secondary atmospheric aerosols, on the other hand, are particulates formed in the atmosphere by gas-to-particle conversion from gases of low volatility. This process will add to the aerosol mass (via heterogeneous condensation) or to the number *and* mass via formation of nanometre sized particles from supersaturated vapour (particle nucleation or new particle formation). Secondary formation typically involves sulphuric acid, nitrates, and several different organic compounds (SOA), which may be of both natural and anthropogenic origin. Atmospheric aerosols often consist of (internal) mixtures of organic and inorganic substances.

The aerosol is polydisperse and distributed between particles of diameters (D_p) spanning several orders of magnitude, ranging from a few nano-meters (nm) up to some 100 micrometers (μm) in diameter. The distribution of the number, surface area or mass of an aerosol population with respect to size can be represented by an aerosol size distribution. The distribution over size of any of the abovementioned moments may be described in terms of one or more log normally distributed size modes. These modes are often termed according to the size ranges in which they appear. As originally suggested by Whitby (1978), they are generally referred to as nucleation mode particles (D_p < ~ 10 nm), Aitken mode (D_p = 10-100 nm), accumulation mode (D_p = 100 nm-1 μm) and coarse mode (D_p > 1 μm).

Each aerosol mode results from specific emissions and atmospheric processes that are influenced by both meteorological and geophysical characteristics. Thus like clouds, aerosol size distributions have distinct shapes, characteristic of the prevailing environment (Clark and Whitby, 1967; Junge, 1969). The comparably fast dynamical and chemical processes acting to transform and deposit the aerosol population result in atmospheric aerosol size distributions, (as well as the aerosol composition and concentration) exhibiting a high degree of spatial and temporal variability. Since an aerosol particle's ability to act as a CCN, among other things depends on its size and chemistry, as well as the size and chemistry of its neighbours (due to competition for water vapour) an accurate description of the size distribution is required to facilitate an accurate representation of cloud formation. Thus, it is important to be able to accurately represent the dynamical processes shaping the aerosol size distribution.

CCN are particles that possess physical and chemical properties favourable to the condensation of water and subsequent cloud droplet growth under atmospheric conditions. The number of available CCN varies depending on the ageing processes and aerosol sources experienced by the air mass. Generally larger particles ($D_p > 50$ nm) are more likely to act as CCN, and in most environments smaller particles ($D_p < 40$ nm) are unlikely to become activated into cloud droplets regardless of their composition (McFiggans et al., 2006). CCN sized particles may be emitted directly at this size range or grow from either a smaller primary particle or a nucleated particle. The uncertainties in the primary emission rates and sizes, although still large, are generally smaller than the uncertainties in the nucleation rates (Pierce and Adams, 2009); therefore, we focus our following discussion on how particles can grow to CCN sizes from the nucleation mode.

The major source of aerosol number in the nucleation mode is particle formation via homogeneous nucleation, and there are several proposed particle nucleation mechanisms that may be significant for particle formation globally (Pierce and Adams, 2009). New particle formation is a research area that has been given a lot of attention during recent years. Much of this work has been oriented towards understanding new particle formation on a process level to facilitate its accurate parameterisation in global climate models (GCMs) (e.g. Kulmala, 2003). Although progress has been made (Kulmala et al., 2007), the mechanism behind particle formation is not fully understood.

New particle formation is often observed as a rapid increase of particles $D_p < 10$nm around noon which subsequently grow into larger sizes during the course of hours to days, so-called nucleation events. These events are episodic in nature and have been typically observed to occur over continental forest sites (Tunved et al., 2006). However, recent measurements show that they are prevalent globally in many other clean or moderately polluted environments, including coastal areas (O'Dowd et al., 2002), upper free troposphere (Singh et al., 2002), cloud outflow regions (de Reus et al., 1999; Twohy et al., 2002), and aged continental plumes (McNaughton et al., 2004). During such events several dynamical processes are active that affect both the number and size of the aerosol. Nucleation mode particles are affected by three key processes. Firstly, dry deposition acts as an important sink of nucleation mode particles near the Earth's surface. The number concentration in the nucleation mode is also very efficiently reduced via coagulation with larger particles, and also self coagulation with particles of similar sizes. The condensation of low volatile vapours onto the nuclei mode also causes them two grow. Therefore, both coagulation and condensation results in a transfer of particle number (via condensation) or mass (via coagulation) from smaller to larger sizes; the particles are not lost but instead re-appear as larger particles in the Aitken mode.

Aitken mode aerosols can also originate from primary emissions during combustion. Coagulation becomes less important and the rate of dry deposition removal also decreases with increasing size in the Aitken size range. During conditions when a lot of condensing material is available, and the pre-existing condensation sink is low (typical of cleaner aerosol environments), the growth of the Aitken mode by vapour condensation can also be traced into the size range of the accumulation mode. However, this process becomes less effective as the particles become larger.

The main growth and removal mechanism that influence abundance and chemistry of particles in the Aitken size range is cloud processing. For non-precipitating clouds these include the scavenging of nonactivated interstitial aerosol (Aitken mode and smaller) and liquid phase reactions within the droplet. Of these two mechanisms liquid phase reactions are thought to be the most effective route of mass transfer to cloud droplets. When the cloud evaporates, the scavenged interstitial particles and heterogeneous reaction products remain in the atmosphere, resulting in an increase in mass of the original nuclei (CCN). The result of the smallest sized particles being activated and growing out of their original size range after a cloud processing cycle leads to the observed Hoppel minimum of the size distribution in the approx D_p = 100nm size range (Hoppel et al., 1994; Bower et al., 1999). When a cloud produces rain, the original nucleation scavenged aerosol (CCN) will be removed. The falling droplets also scavenge particles below the cloud base.

Therefore, the efficiency by which nucleated particles reach climatically-relevant sizes essentially depends on two competing factors: the growth rate and the scavenging by various removal processes (Kerminen et al., 2001; Lehtinen et al., 2007). The combination of removal of aerosols by in-cloud and below-cloud scavenging is generally termed wet deposition. Thus, it is clear that clouds and aerosols are deeply interlinked via the effects they exert on each other, meaning that changing the properties of the aerosol will affect the properties of the cloud and precipitation and vice versa.

Accumulation mode particles originate from the emission of primary particles or growth of smaller particles. Within this size range the removal by dry deposition is at a minimum (Slinn et al., 1978). Therefore, compared to smaller and larger sized particles, accumulation mode particles have a long residence time in the atmosphere (up to weeks). The only mechanisms significantly altering the properties of particles in the accumulation mode is cloud processing and/or wet deposition. An overview of processes involved in the aerosol lifecycle is provided in Figure 2.

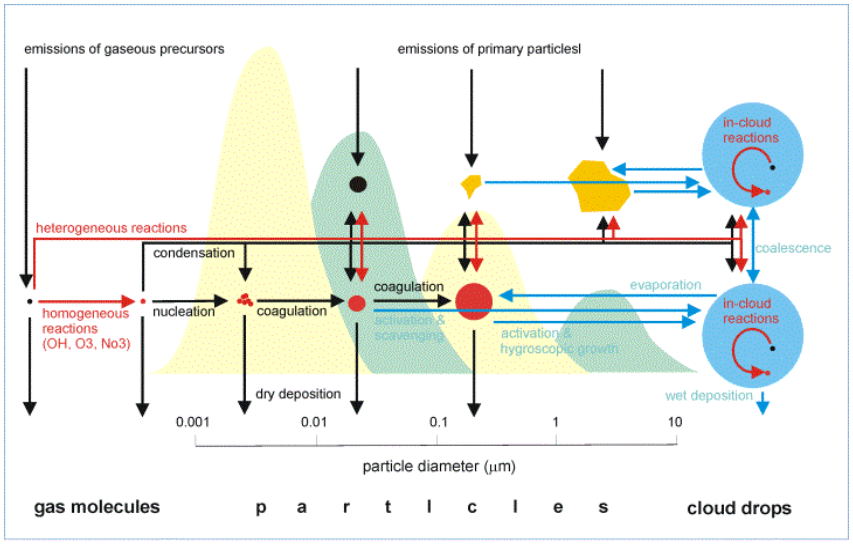

Figure 2: Overview of microphysical mechanisms influencing the atmospheric aerosol over different size ranges. The aerosol population is influenced by homogeneous, heterogeneous and in-cloud reactions. Numerous different compounds participate in condensation growth of particles: From Raes et al., 2000.

With regard to their influence on cloud formation, the accumulation mode is recognised as the most important aerosol mode as it is the dominant source of CCN. The relative contribution of particles to the accumulation mode, and thus CCN, from either primary emitted particles or growth from the nucleation mode depends principally on the how polluted the aerosol environment is. Primary emitted particles enter the atmosphere generally at much larger sizes (diameters at least 10nm or greater) than the size of nucleated particles, meaning that emitted particles affect CCN concentrations more directly than do nucleated particles (Pierce and Adams, 2009). This means that primary particles dominate CCN concentrations near regions of primary particle emissions (Adams and Seinfeld, 2003).

In cleaner environments, it has been proposed that nucleation and subsequent growth to climatologically important CCN sizes is a dominant pathway for the formation of CCN (Pirjola et al., 2002; Laaksonen et al., 2005). Moreover, recent field campaigns have shown that a significant fraction of cloud droplets activate on ultrafine (<100nm) particles, especially for aerosol environments which are clean and CCN limited (Glantz et al., 2003; Komppula et al., 2005; Kerminen et al., 2005).

Determining an accurate picture of the global CCN distribution is however just one component of the climate system required to describe the climate forcing of aerosols. To assess how CCN affect cloud properties, a detailed understanding of cloud nucleating ability of CCN is required which will be the focus of the next section.

1.3 Cloud-Aerosol interaction

A subset of the atmospheric aerosol discussed in Section 1.2 serve as CCN upon which water vapour condenses to form cloud droplets at the supersaturations achieved within clouds. Recently there has been an increasing focus towards improving our understanding of the processes by which anthropogenic emissions of aerosols can alter the radiative properties of clouds via modifying their microphysical and macrophysical properties. These indirect effects were summarized in Section 1.1, and a schematic picture of the various proposed mechanisms is provided in Figure 3. From the numerous mechanisms illustrated we will focus our discussion on the first indirect effect (or cloud albedo effect) on *warm liquid phase* clouds highlighted by the red box in Figure 3. The cloud albedo is a measure of the fraction of incident shortwave (solar) radiation reflected by the cloud and is dependent on the cloud depth, cloud fraction, liquid water content and cloud droplet number concentration (CDNC).

In order to accurately evaluate the impact of pollution on the global climate via indirect aerosol effects we need a detailed understanding of the cloud albedo susceptibility to perturbations in the ambient aerosol concentration (Platnick and Twomey, 1994; Ackerman et al., 2000).

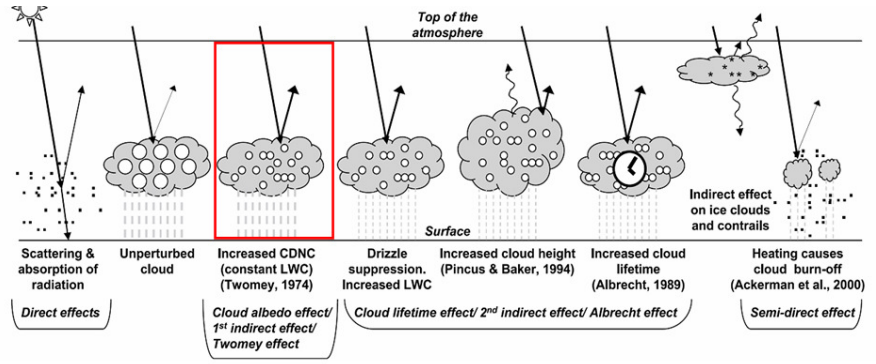

Figure 3: Various mechanisms identified by which aerosols can significantly alter the physical properties and formation of clouds. CDNC stands for "cloud droplet number concentration" and LWC stands for "liquid water content": From Haywood and Boucher, 2000.

In the absence of other changes, the clouds with visible albedo close to 0.5 (characteristic of marine Stratocumulus) that have relatively low droplet concentrations are especially susceptible to perturbations in cloud-drop number concentrations, and by inference, the atmospheric aerosol (Twomey 1974, 1977; Charlson et al., 1987). The most visible alteration of Stratocu-

mulus (Sc) clouds albedo via local aerosol perturbations has been observed via the injection of particles associated with ship exhaust causing "tracks" in the clouds, i.e. linear regions of locally higher aerosol particle and cloud droplet concentrations and greater cloud reflectivity (Radke et al., 1989; Durkee et al., 2000). Figure 4 shows a satellite image of ship tracks over the Northeast Pacific obtained during the 1994 MAST (Monterey Area Ship Track) experiment.

In addition, Sc are important modulators of the Earth's radiation budget due to their frequency of occurrence, extensive spatial coverage (annually 18% over land and 34% over oceans, Warren et al., 1986a,b), long synoptic life time, relative statistical homogeneity at the mesoscale and reproducible diurnal cycle (Brenguier and Wood, 2009). In addition, oceans have a lower albedo than continents and so there is a greater albedo contrast between cloud and surface in maritime areas (e.g. see Figure 4). Consequently there is greater climate sensitivity to aerosol perturbations for marine Sc compared to continental Sc. The combination of their high susceptibility to aerosol perturbations and climatological importance has made marine Sc the basis for numerous studies, and these clouds will also be the focus of this thesis.

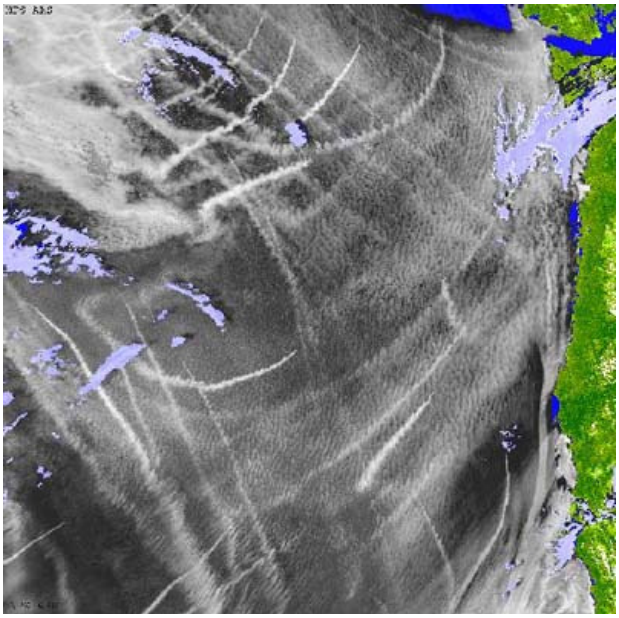

Figure 4: Advanced Very High Resolution composite image taken at 22:45 UTC on June 27th, 1994. Source: Remote sensing Laboratory, Naval Postgraduate School, Monterey, CA.

Currently a large part of the global atmosphere is not well characterized with respect to cloud susceptibility, i.e. the relative sensitivity of cloud properties to aerosol perturbations, due to a lack of measurements and an incomplete understanding of the pathways through which aerosol perturbations manifest themselves on the climate system via clouds. This has frustrated attempts to develop simplified parameterizations of indirect processes required for regional and global models, yet these modeling tools are relied on heavily for estimating aerosol indirect effects.

A primary debate concerning the aerosol indirect effect revolves around the degree to which pollution contributes to the particle number concentration at diameters > 50 nm (i.e. CCN size), and the subsequent extent to which the total cloud droplet number (N_d) increases with increasing aerosol. As the CDNC for Sc is determined directly at cloud base, it is vital to improve our understanding of how meteorological characteristics and aerosol properties influence activation of aerosols at cloud base (Wex et al., 2008).

Hygroscopic growth and activation of aerosol particles to form cloud droplets is a critical component of aerosol-cloud interaction. The theoretical framework that describes these processes is the Köhler equation, which connects the water vapour saturation above the surface of a droplet to the droplet diameter. Köhler (1936) determined the equilibrium vapour pressure above small solution droplets by combining the Kelvin equation with Raoult's law. The Kelvin effect describes the increase of water vapour saturation due to the curvature of the droplet. The Raoult term accounts for a lowering of the water vapour saturation due to the soluble substance in the droplet.

Köhler theory states that if a droplet grows to a size that exceeds its so called critical radius, it is said to be activated. The activation of a given particle requires that the ambient supersaturation exceeds a critical value, which depends on the dry particle size and chemical composition. The critical supersaturation decreases with increasing particle radius or with increasing mass of soluble substance contained in an internally mixed particle. Larger particles with a larger soluble mass fraction are more likely to act as CCN. The effects of composition on activation are greatest in the size range 40-200nm. Only a fraction of the particles can grow beyond their critical radius to form droplets. When unactivated the remaining particles exist as interstitial aerosol in the cloud. In summary the ability of particles to act as a CCN is a function of the size of the particles, their composition and mixing state, and the supersaturation of the air (Fitzgerald, 1974; Hegg and Larson, 1990; Laaksonen et al., 1998; Feingold, 2003; Kanakidou et al., 2005; Quinn et al., 2008).

Thus, the adequate treatment of particle activation in warm clouds must take into account the aerosol number concentration, its chemical composition and the supersaturation reached within the air parcel. Previous studies have shown that the updraft velocity has a strong influence on the number and size of cloud droplets formed (Feingold, 2003; Rissman et al., 2004).

Higher updrafts result in higher water vapour supersaturation which is the driving force for condensational growth. Thus in order to assess the sensitivity of CDNC to aerosol perturbations the effect of the prevailing meteorology must be considered. A common way of examining this is through sensitivity studies using cloud models.

1.4 Sensitivity studies: liquid phase clouds

Cloud models ranging in complexity from parcel models up to a full 3D treatment of the cloud micro- and macrophysical structure are currently available. The most fundamental form of a cloud model is the adiabatic cloud parcel model. Such cloud models predict cloud droplet concentrations within ascending air parcels by simulating the transfer of water vapour and heat between the adiabatic cooling air parcel and the CCN using a first principles treatment of chemical and thermodynamic processes. The representation of the growth of an aerosol population in the current generation of adiabatic cloud models (Feingold and Chuang, 2002; Nenes et al., 2002; Roelofs and Jongen, 2004) are similar to the first models used to investigate the effects of aerosols on clouds (Howell, 1949; Mordy, 1959). Adiabatic cloud parcel models typically employ a moving centre approach for the numerical representation of the particle size distribution (Jacobson, 1997; Korhonen et al., 2005). This approach eliminates numerical diffusion and allows for a smooth transition from aerosol to cloud droplets without artificial distinction between these classes. This moving centre based structure has been shown to most accurately reproduce the qualitative features of the size distribution (Zhang et al., 1999). In this paper such models are employed and therefore they will be the focus of our subsequent discussion (for warm clouds).

Untangling the relative importance of the aerosol physiochemical properties (including size, chemical effects such as composition, surface tension and accommodation coefficient, as well as meteorology -updraft velocity) for the cloud nucleating ability of aerosol particles is at present a major challenge facing the cloud-aerosol modelling community, and this topic is at the core of the aerosol indirect effect (Dusek et al., 2006; McFiggans et al., 2006; Andreae and Rosenfeld, 2008; Stevens and Feingold, 2009).

Modelling studies by Feingold (2003) and Ervens et al. (2005) showed that for an internally-mixed aerosol, composition has a relatively small effect on droplet activation compared to aerosol parameters such as particle concentration and size, and dynamical parameters such as the updraft velocity, except perhaps under conditions of both high pollution levels and small updraft velocities. Dusek et al. (2006) concluded that the cloud nucleating ability of particles was largely controlled by size, and that composition plays

a secondary role. This is in agreement with previous studies (Junge and McLaren, 1971; Fitzgerald, 1973). In the study by Dusek et al. (2006) they concluded that showed that particle size accounts for 84 to 96% of observed variability in CCN concentrations. However, Hudson (2007) presented a more extensive set of measurements that showed significantly more variability in the relationship between dry particle size and critical super-saturation by including cleaner air masses in the analysis. Other studies have also shown that under certain combinations of meteorological/aerosol conditions the effect of chemistry may be relatively more important (e.g. Lance et al., 2004; Rissman et al., 2004; Twohy et al., 2008).

The surface tension is also a highly uncertain parameter. The presence of organic surface tension-lowering compounds in the aerosol (Facchini et al., 1999; Gautam and Tyagi, 2006) which enhance droplet activation by decreasing the droplet surface tension; and surface forming organic films (Feingold and Chuang, 2002) are acknowledged as important "uncertain" contributors to cloud formation. The value of the mass accommodation coefficient is widely acknowledged to be uncertain, experimentally determined values ranging from 0.01 to 1.0 (Xue and Feingold, 2004 and references therein). Chemical effects have also been associated with a broadening of the droplet size distribution. Examples of these effects include the possible role of nitric acid (Xue and Feingold, 2004) and the existence of condensation inhibiting compounds (Feingold and Chuang, 2002). The surface tension has also been shown to contribute to dispersion of the droplet size distribution (Srivastava, 1991). The effects of these chemical parameters on droplet activation individually and in combination are not well understood.

In addition, Köhler theory assumes equilibrium growth of a particle which may not be realistic in certain situations. Kinetic limitations may therefore further complicate the description of the droplet activation and growth processes (Chuang et al., 1997; Nenes et al., 2001).

A question remains whether the contrasting relative sensitivities found in models can be attributed to a misrepresentation of the balance of processes mentioned above. The difficulty in unravelling relationships among aerosols, clouds and precipitation has been attributed to the inadequacy of existing tools and methodologies (Stevens and Feingold, 2009). Numerous cloud-aerosol modelling sensitivity studies have been conducted; however, many of these studies to date have been "local", i.e. investigating parameter sensitivity in the vicinity of their actual values. Ervens et al. (2005) examined numerous chemical/composition effects in unison and showed that due to compensation between parameters the effect of composition on total droplet number was significantly less than suggested by studies that address the effects individually. Few studies have used statistical analysis tools to investigate the global sensitivity of a cloud model to input aerosol parameters in order to treat the (non-linear) interaction between all parameters over the entire parameter space simultaneously. One example is the study of Anttila

and Kerminen (2007), which used the probabilistic collocation method (PCM) to test the global sensitivity of cloud microphysics to Aitken mode particles (50-100 nm diameters). Global sensitivity analysis considers parameter changes over the entire multi-dimensional parameter domain. This generally leads to different, but more reliable results because parameter sensitivities in nonlinear models typically vary considerably over the feasible space of solutions.

1.5 Closure studies: liquid phase clouds

The ultimate test for prognostic parameterizations and cloud models is the comparison of their predictions against comprehensive in situ data. To ascertain the inadequacy/adequacy of different process descriptions within models and how these descriptions affect the derived aerosol-cloud sensitivity, it is paramount to perform closure studies, e.g. aerosol-CCN or CDNC closure refers to a comparison of measured and predicted CCN or CDNC concentrations where the model predictions are derived from measured inputs (e.g. aerosol size distributions). Robust closure relies on in-situ measurements with high temporal and spatial resolutions.

Numerous studies have applied Köhler theory in combination with measured hygroscopic growth properties of particles to derive the critical supersaturation that corresponds to the activation of these particles into droplets. The accuracy of the treatment of activation within models has been investigated via aerosol-CCN closure studies for both laboratory generated aerosol particles (e.g. Brechtel and Kreidenweis, 2000; Koehler et al., 2006) and *in-situ* gathered atmospheric aerosol particles (e.g. Chuang et al., 2000; Dusek et al., 2003; Ervens et al., 2007). Generally *in-situ* atmospheric aerosol-CCN closure studies have had limited success. The largest discrepancies were found in the presence of aerosol strongly influenced by anthropogenic sources, having high concentrations of organic carbon in the aerosol phase (Broekhuizen et al., 2006). Thus, the disagreement has usually been attributed to an incomplete understanding of the aerosol composition and the degree of internal mixing; especially the role of organic species (Stroud et al., 2007) as well as surface tension effects (Wex et al., 2008). The difficulties in obtaining closure between the observed and calculated CCN highlights possible shortcomings in the current state-of-the-art knowledge concerning the impacts of chemical composition on the CCN number, or the measurement techniques used to derive the CCN spectrum.

However, even if a full aerosol-CCN closure was to be achieved this still does not necessarily mean that we know the actual cloud microphysical response to changes in the atmospheric aerosol as this will vary for different

meteorological conditions (Section 1.4). To obtain this type of information, it is necessary to perform an aerosol-CDNC closure (often termed droplet closure) using a cloud model. Adiabatic cloud parcel models have been evaluated against in-situ observations to estimate the impact of aerosol number/size/composition for liquid clouds (Ayers and Larson, 1990; Nenes et al., 2002; Hsieh et al., 2009). Such approaches assume the computation of the CCN spectrum as an intermediate step implicit in the calculations (Conant et al., 2004). The success of these closure studies for a number of different measurement campaigns has been wide-ranging. For instance approx 50% discrepancy between simulated and measured droplet concentrations was found for continental Sc clouds (Hallberg et al., 1997), and a similar disagreement was observed for the second Aerosol Characterization Experiment (ACE-2) for marine Sc clouds (Snider and Brenguier, 2000; Snider et al., 2003). In other closure studies, (Conant et al., 2004; Meskhidze et al., 2005; Fountoukis et al., 2007) much better agreement between modelled and measured droplet concentrations have been found.

In agreement with aerosol-CCN closure studies, aerosol-CDNC studies have generally been more successful when they have been associated with clouds formed in cleaner aerosol conditions. However, untangling the contribution of limitations in the observations from incomplete model process descriptions remains a challenge. This is further complicated by uncertainties in the dynamical representation of clouds. Fountoukis et al. (2007) found the correlation of droplet error to be high for the updraft velocity (which they used as a proxy for cloud dynamics) and that this error increased with decreasing updraft velocity. They did not find any correlation of droplet error with variations in chemical composition, thus highlighting dynamical effects may be more important for accurately predicting cloud properties than aerosol chemistry.

One area of research related to the inadequacy of current parameterisations of droplet formation is their ability to represent the width of the droplet spectrum, typically indicated by the relative dispersion (D). This shortcoming has been advocated to be a source of larger uncertainty in current estimates of the aerosol indirect effect (Liu and Daum, 2002; Liu et al., 2008; Rotstayn and Liu, 2003; Zhao et al., 2006).

The width of cloud droplet spectra observed in Sc have been shown to be difficult to reproduce numerically due to the varying spatial and temporal scales over which different processes simultaneously occur within the cloud layer. Current predictions of droplet size distributions from condensational growth theory fail to represent the broadness of droplet size distributions observed in clouds (Yum and Hudson, 2005). For instance Hsieh et al., 2009 found that the parameterisations commonly applied in adiabatic cloud parcel models could essentially capture one-dimensional dynamics; however the predicted droplet size distributions were too narrow. Changes in the cloud droplet spectrum can be attributed to entrainment and subsequent cloud dilu-

tion (Derksen et al., 2009); the presence of giant CCN, additional nucleation of cloud droplets above the cloud base associated with an increase in updraft velocity (Pinsky and Khain, 2002); turbulence effects, collision-coalescence of cloud droplets and drizzle formation (Feingold et al., 1996; Shaw et al., 1998; Kostinski and Shaw, 2005); circulation mixing associated with the presence of localised downdraft regions surrounding broader updraft regions (Lu et al., 2009; Wang et al., 2009 and references therein); variable updraft velocities (Hudson and Svensson, 1995; Hudson and Yum, 1997); and also instrument artefacts (Hsieh et al., 2009 and references therein).

Large scale models typically apply some form of parcel theory for computing cloud droplet spectral properties (Nenes and Seinfeld, 2003; Hsieh et al., 2009). From our discussion above regarding the limited success of closure using parcel models, it follows that the poor understanding of clouds haunts not only attempts to represent aerosol effects observationally, but also numerically on larger scales (Brenguier and Wood, 2009). These problems cast doubt on the use of large scale models to quantify the climate forcing due to small scale perturbations, as the results can be expected to be heavily dependent on the (often flawed) conceptual framework underlying a particular parameterisation (Brenguier and Wood, 2009).

It is therefore paramount to devise new strategies to ensure the physical basis of existing models is sound, and able to represent key droplet activation processes with accuracy. With this in mind it would be beneficial to have tools that could in a statistically robust manner perform droplet closure and global sensitivity in a unified framework to help guide modellers and measurements towards key parameters and processes which have the highest uncertainty.

2. Scientific goals of the thesis

New methodologies are required to unravel the complex interplay between clouds and aerosols.

- The primary scientific goal of the work presented in this thesis is to improve the understanding of cloud-aerosol interactions through developing and testing whether inverse modeling approaches constitute an efficient set of tools for evaluating process descriptions in adiabatic cloud models.

The work is divided into sub-goals, each one encompassed by the publications and manuscripts upon which this thesis builds.

As previously discussed, neither aerosols nor clouds can be considered as entities isolated from each other. Difficulties in describing the climate effects induced by aerosols via cloud formation and modification may be located both in the spatial and temporal representation of the aerosol, as much as in the description of the actual cloud formation itself. In other words, if we lack the ability to accurately describe the aerosol; the level of confidence placed in the predicted cloud properties will typically be low. Thus in the first paper of this thesis we develop a new Lagrangian box model framework and apply state-of-the art knowledge of aerosol dynamical processes to pinpoint the relative importance of sources and transformation pathways of the atmospheric aerosol. The main scientific goal of paper I is to:

- Evaluate the accuracy of current state-of-the-art model descriptions of aerosol source and sink processes by comparing simulated aerosol properties against their measured counterparts at the SMEAR II station in the Finnish boreal forest.

Subsequent papers II-IV relate to the development and application of an inverse modeling approach to investigate cloud droplet forming processes. The main scientific goals of these papers are to:

- Ascertain whether inverse modeling provides a transparent and efficient means of probing cloud aerosol interactions by coupling a pseudo-adiabatic cloud parcel model to automatic search algorithms.
- Confirm that a state of-the-art Markov Chain Monte Carlo (MCMC) algorithm can successfully solve the cloud-aerosol inverse problem, while simultaneously providing estimates of parameter sensitivity and correlation.
- Evaluate the applicability and power of MCMC simulation to provide a global sensitivity analysis of the parameters describing the aerosol physiochemical properties and meteorology.
- Demonstrate that a MCMC simulation provides a statistically robust and detailed means of efficiently testing the performance of adiabatic cloud models against in-situ observations of cloud properties.
- Demonstrate that the MCMC approach adds value to traditional aerosol-cloud droplet size distribution closure methodologies.

With this inverse modeling framework to investigate cloud aerosol interactions we will:

- Pinpoint which are the dominant parameters controlling the activation of cloud droplets for clouds experiencing different updraft velocities; over a range of different aerosol environments.
- Provide a measure of the discrepancy between the model and in-situ measurements of cloud droplet size distributions as a function of the aerosol physiochemical parameters and updraft velocity for marine Sc clouds.
- Suggest improvements of both modeling approaches as well as measurement strategies relating to aerosol cloud interactions.

3. Methodology

Two separate modeling approaches were developed in this thesis to probe aerosol transport, evolution, and cloud-aerosol interactions. This split allows us to apply the appropriate modeling frameworks to the two different process scales considered in this work. A schematic of the overall modeling framework is shown in Figure 5.

3.1 Process models

In paper I the evolution of a particle population is simulated using a new trajectory-driven aerosol and chemical process model: Chemical and Aerosol Lagrangian Model (CALM). The position of CALM within our overall modeling framework is depicted by the grey dashed box (Figure 5). The main aerosol dynamical processes accounted for in the model are simulated using the University of Helsinki Multicomponent Aerosol model (UHMA) described in detail by (Korhonen et al., 2004). The current model setup adopts a two layer box model structure with a residual and mixing layer. The residual layer height is fixed throughout the simulation and is determined by the maximum mixing layer (ML) height during the simulation. CALM is driven along trajectories which determine the transport of these internally well-mixed boxes. In this study the trajectories are calculated using HYSPLIT4 (Draxler and Hess, 1997).

In papers II-IV we move to smaller scales and single out the process of CCN activation and condensational growth above the cloud base for a more detailed analysis using a separate pseudo adiabatic cloud parcel model (Roelofs and Jongen, 2004). The positioning of this model within our overall framework is shown in the left partition of the red box (Figure 5). This model is a similar type to the adiabatic cloud parcel model used in the CALM model (purple box).

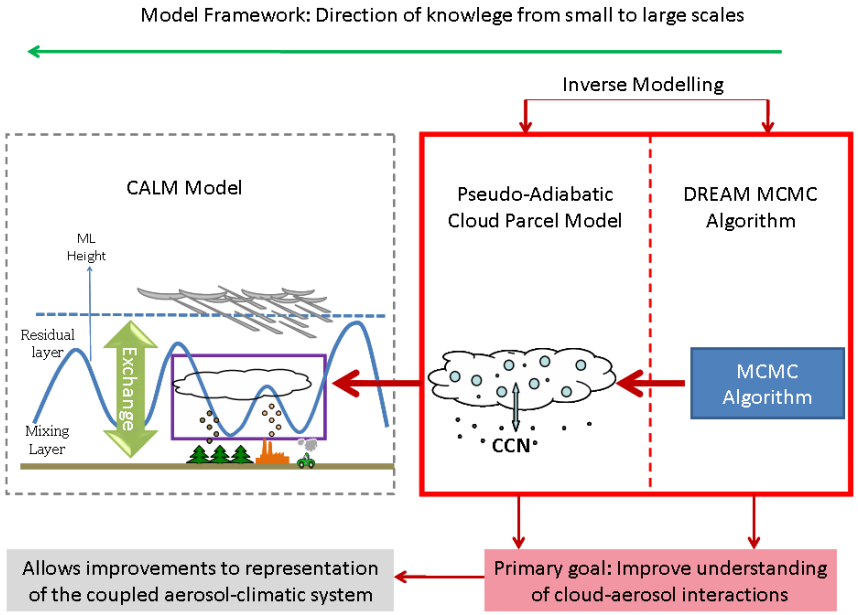

Figure 5: Schematic picture of the modeling framework employed: The grey dashed box is a conceptual box representation of the CALM model moving along the *x*-direction. The purple box within the CALM framework represents the adiabatic cloud parcel model used in CALM. The red box represents the pseudo-adiabatic cloud model and algorithm used in our inverse modeling framework. Within this red box the partition to the right of the dashed red line contains the state of the art MCMC algorithm (DREAM). This is coupled to a pseudo-adiabatic cloud model which is of a similar type used in CALM (partition to the left of the dashed red line).

3.2 Introduction to inverse modeling

One approach to the analysis of cloud-aerosol interactions is to embrace inverse modeling to scrutinize and evaluate model parameter interactions over a wide range of input and output conditions. In inverse analysis, a given model is calibrated by iteratively changing input values until the simulated output values match the measured data as closely and consistently as possible (parameter estimation). Inverse modeling provides a means to achieve this, and is generally based on some type of least squares or maximum likelihood criterion (Vrugt et al., 2008). Bayesian inference represents a mathematically rigorous approach to parameter estimation. This statistical method treats the model parameters as random variables with a joint (but yet unknown) posterior probability distribution (i.e. the estimated distribution of the retrieved parameters). In the past few decades, MCMC simulation has

become a standard computational method for performing Bayesian statistical analyses. In this approach the posterior distribution is described as a combination of prior information and the evidence within the measurements. Thus, this approach allows us to invoke posterior probability density functions of our pseudo-adiabatic cloud model parameters.

The MCMC scheme was introduced by Metropolis et al. (1953). The basis is a Markov chain, which generates a random walk through the search space and successively visits solutions stemming from a fixed probability distribution (Vrugt et al., 2009a). The original Metropolis MCMC scheme was extended for posterior inference in a Bayesian framework by Gelfand and Smith (1990), and has subsequently enjoyed widespread use in many fields of study (San Martini et al., 2006; Vrugt et al., 2009b and references therein; Järvinen et al., 2010). Such methods do not only provide an estimate of the best parameter values, but also a sample set of the underlying (posterior) uncertainty i.e. the full probability distribution function of the solution in the n dimensional model parameter space, where n equals the number of parameters to be estimated. This distribution contains important information about the global parameter sensitivity, and correlation (interaction), and can be used to produce confidence intervals on the model predictions as well as aid in diagnosing structural inaccuracies of the model being tested.

3.3 Automatic search algorithms

In paper II the inverse modeling framework that is used in this thesis (solid red box in Figure 5) involves coupling the pseudo-adiabatic cloud parcel model to a deterministic optimisation algorithm: the Shuffled Complex Evolution global optimisation algorithm (SCE-UA) (Duan et al., 1992) to introduce an automatic parameter estimation framework to solve the cloud - aerosol inverse problem. The SCE-UA algorithm locates the optimal solutions but does not provide an estimate of the underlying parameter uncertainty, associated with model nonlinearity, measurement and model error.

In papers III and IV we couple the same pseudo-adiabatic cloud parcel model to a state-of-the-art DiffeRential Evolution Adaptive Metropolis (DREAM) MCMC algorithm (Vrugt et al., 2008, 2009a). This allows us to approximate the posterior parameter distribution. The positioning of this algorithm in our framework is shown in the right partition of the red box (Figure 5).

A schematic of the cloud-aerosol inverse modeling framework used in papers II-IV that corresponds to the large red box in Figure 5 is illustrated in Figure 6.

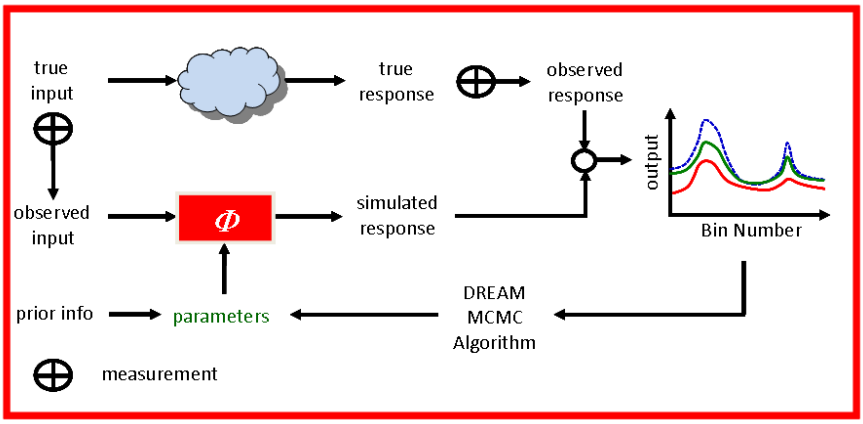

Figure 6: A schematic representation of inverse modeling. The rectangular box in the bottom panel Φ represents the pseudo-adiabatic cloud model that is being used to predict the observed particle size distribution from given input data (also called forcing or boundary conditions), and some *a-priori* values of the model parameters (e.g. lognormal parameters describing aerosol size distribution, soluble mass fraction, updraft velocity). These model parameters are iteratively adjusted so that the predictions of the model, Φ (represented by the green and red solid lines) approximate as closely and consistently as possible the observed response (measured particle size distribution). We focus on the activated (droplet) region of the particle size distribution only.

3.4 Measurement sites

In paper I the CALM model was tested and evaluated against observations performed at the SMEAR II station located at Hyytiälä in Finland (Kulmala et al., 2001).

To benchmark our cloud-aerosol inverse modeling framework, the analysis in papers II and III is performed with synthetically generated cloud droplet size distributions simulated using average aerosol size distribution measurements from the literature. To test a wide range of input aerosol size distributions, data from four distinctively different aerosol environments were used:

1. Marine Arctic: Ny-Ålesund, Svalbard (P. Tunved, personal communication, 2011).
2. Marine average: Taken from a compilation of measurements of marine aerosol (Heintzenberg et al. 2000).
3. Rural continental: SMEAR II station at Hyytiälä (Tunved et al. 2005).
4. Polluted continental: Melpitz station (Birmili et al., 2001).

In the final paper presented in the thesis (IV) we repeat the inverse modeling approach developed in papers II, III, this time using real measurements of aerosol physiochemical and droplet size distributions from the MASE II (Marine Stratus/Stratocumulus Experiment) field campaign undertaken over the eastern Pacific Ocean off the coast of central California during July 2007 (Hersey et al., 2009; Lu et al., 2009), (Figure 7).

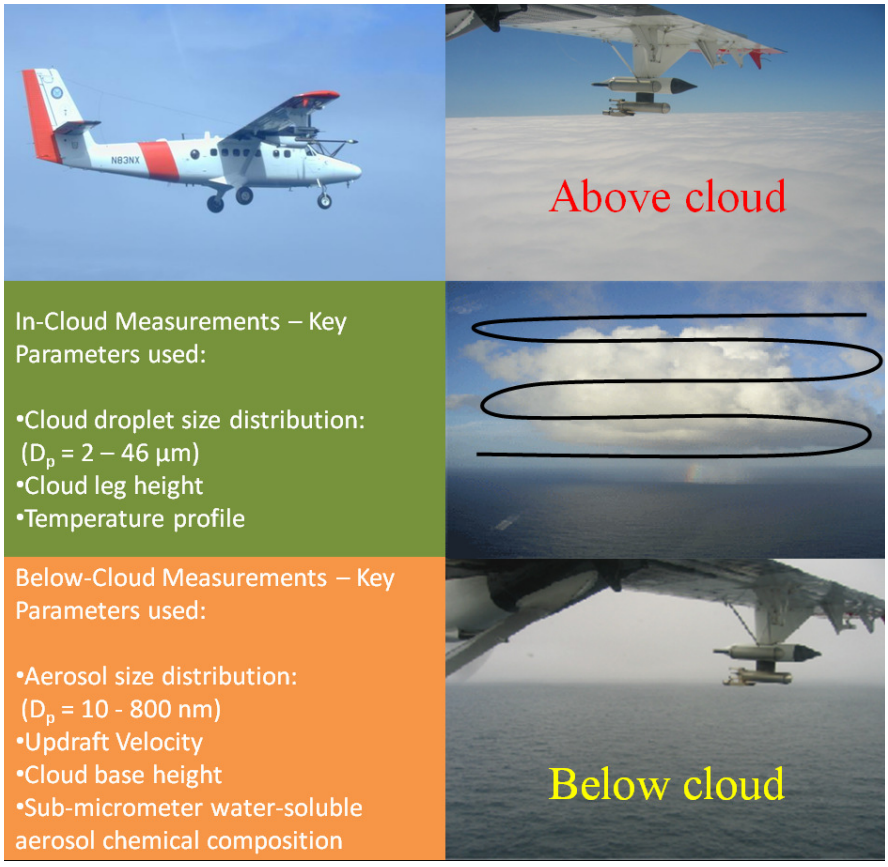

Figure 7: Outline of in-cloud and below cloud measurements used from the flights performed in the MASE II field campaign using instrumentation onboard the Center for Interdisciplinary Remotely-Piloted Aircraft Studies (CIRPAS) Twin Otter: Pictures courtesy of Armin Sorooshian, personal communication 2010.

4. Summary of Papers

4.1 Paper I: New trajectory-driven aerosol and chemical process model: Chemical and Aerosol Lagrangian Model (CALM)

The aim of this study was to benchmark a new trajectory driven Lagrangian process model (CALM) that seeks to capture and describe the processes that govern the evolution of aerosol chemical and physical properties along trajectories and at receptor sites. In this paper, it was shown that CALM is capable of reproducing annual and diurnal cycles at the SMEAR II station in Hyytiälä, Finland with satisfying accuracy. The model was also used to study the contribution of new particle formation versus primary particle production at Hyytiälä, as well as the role of Biogenic Volatile Organic Compounds (BVOC) emissions for the provision of particle number and mass. It was shown that anthropogenic primary emissions (from the European subcontinent) determine the particle number concentration (CN) at Hyytiälä when advection from the south occurs. However, when transport of relatively cleaner marine air takes place, the CN is governed by new particle formation. During these transport conditions, biogenic emissions from the boreal forest were shown to be essential in providing precursors of condensable material to sustain growth of the freshly formed aerosol particles. These results corroborate previous findings (Spracklen et al., 2006). Clouds, as described in CALM, play an important role in regulating especially the accumulation mode concentration. By cancelling clouds and precipitation, the number of accumulation mode particles is substantially increased.

The CALM model is currently undergoing more extensive testing on the European sub-continental scale and can in future be used for studies of regional scale transport as well as serving as reference model in evaluating more simplified aerosol schemes in large-scale transport models. The CALM model may also be used to evaluate the performance of new parameterizations, for instance, newly developed new particle formation schemes.

4.2 Paper II: Inverse modeling of cloud-aerosol interactions – Part 1: Detailed response surface analysis

The purpose of this paper was to introduce the application of inverse modeling to cloud-aerosol interactions using a pseudo-adiabatic cloud parcel model. The gradient change in objective function (OF), containing the difference between the measured and model predicted droplet size distribution, is presented in two-dimensional plots termed response surfaces.

The response surfaces were used to investigate the posedness of the cloud-aerosol inverse problem, whilst simultaneously providing a graphical illustration of the susceptibility of simulated droplet size distributions to changes in the updraft velocity and aerosol physiochemical parameters. For each aerosol environment the most important parameter was shown to be the updraft velocity. It was shown that the susceptibility of the cloud droplet size distribution to perturbations in these parameters is higher in cleaner marine Arctic aerosol environments compared to polluted continental environments. Corroborating previous studies, e.g. Nenes et al, 2002, a reduction in particle concentrations had a small effect on the cloud microphysical properties for polluted regions, whilst clean regions such as marine and marine Arctic environments are much more responsive to changes in aerosol physiochemical properties and abundance. A shift towards an increase in the importance of chemistry (denoted by the soluble mass fraction) compared to the concentration of accumulation mode number concentration was shown to exist somewhere between marine (~75 cm^{-3}) and rural continental (~450 cm^{-3}) aerosol regimes. Therefore, it is important to provide accurate measurements of the aerosol chemical composition for polluted environments for the accurate simulation of cloud microphysical properties.

When investigating the posedness of the inverse problem certain parameters are found to be non-identifiable. That is, the information content stored within the OF does not warrant their estimation using inverse modeling. It was demonstrated that including the interstitial aerosol in the OF constrained the solution to the inverse problem for the lognormal parameters describing the smaller Aitken mode.

Many of the parameters exhibited highly non-linear interactions. These correlations indicate regimes where compensating effects may produce almost identical droplet distributions as in the base case. This highlights the need to apply MCMC methods that treat the interaction between all parameters involved in cloud droplet activation simultaneously for a robust sensitivity analysis.

4.3 Paper III: Inverse modeling of cloud-aerosol interactions – Part 2: Sensitivity tests on liquid phase clouds using a Markov Chain Monte Carlo based simulation approach

The purpose of this paper was to demonstrate the applicability of MCMC simulation for determining the global sensitivity of parameters describing the aerosol physiochemical properties of a pseudo adiabatic cloud parcel model. This allows a comparison of our 2D response surface analysis (paper II) to the parameter sensitivity in the full multi-dimensional parameter space of the system.

To a large extent, results from prior studies were confirmed (e.g. Feingold, 2003; Lance et al., 2004; Antilla and Kerminen, 2007; Quinn et al., 2008), but the present study also provided some novel findings. In agreement with paper II there is a clear transition in the inverse modeling results from very clean marine Arctic aerosol conditions to polluted continental (aerosol concentration in the accumulation mode > 1000 cm^{-3}). In clean environments the aerosol parameters representing the mean radius and geometric standard deviation of the accumulation mode were found to be most important for determining the cloud droplet size distribution whereas particle chemistry was more important than both number concentration and mean size of the accumulation mode for polluted continental aerosol conditions. Further simulations were performed to investigate the effect of the base updraft velocity on the parameter sensitivity which showed that the relative sensitivity of the chemistry is a strong function of the prevailing meteorological conditions and number of accumulation mode particles.

We also highlight the strong competition and compensation between the cloud model input parameters, illustrating that if the soluble mass fraction is reduced, both the number of particles, geometric standard deviation and the mean radius of the accumulation mode must increase in order to achieve the same cloud droplet size distribution. This result suggests that for the cloud parcel model used herein, the relative importance of the soluble mass fraction appears to decrease if the number or geometric standard deviation of the accumulation mode is increased. Strong interactions exist between all of the parameters investigated over the range of possible solutions, and these are observed to more non-linear for more polluted aerosol conditions. Our results highlight that clouds are complex, multidimensional problems that may have a plethora of possible solutions due to compensating effects.

4.4 Paper IV: A study of marine stratocumulus clouds using an inverse modeling approach

The goal of this study was to present a new framework where cloud models can be combined with in-situ measurements of cloud properties to efficiently and in a statistically robust manner assess the global sensitivity of the droplet size distribution to the aerosol physiochemical and meteorological (calibration) parameters. The method simultaneously provides a detailed assessment of aerosol-cloud droplet size distribution closure procedure and transparently examines the suitability of the pseudo-adiabatic cloud parcel model to comprehensively describe the evolution of cloud droplet size distributions in Sc clouds. We used the same setup as in paper III but instead of synthetic data, we used measurements of both below cloud aerosol and meteorology as well as measurements of droplet size distributions (calibration data) for four marine Sc clouds measured during the MASE II campaign.

As in paper II we demonstrate that the updraft velocity is the most important parameter for describing the observed droplet distribution for the cloud cases studied. The modeled droplet size distribution is shown to be more sensitive to the number, size and shape of the accumulation mode aerosol compared to the soluble mass fraction for all cloud cases except the most polluted (number concentrations of accumulation mode: ~450 cm^{-3}). Thus our results highlight that under anthropogenic influence, we must consider chemistry also in marine environments; climate models should not ignore chemical composition, which is in agreement with recent studies (e.g. Roesler and Penner, 2010).

The MCMC algorithm successfully matches the observed droplet size distribution for each cloud case. However, there is relatively poor agreement between the simulated and measured calibration parameters involved in the optimisation procedure, especially for the updraft velocity, mean radius and geometric standard deviation of the accumulation mode. The probability densities of the solutions for these three parameters are skewed away from the median measured values to the limits of their respective posterior distributions. This informs us that either there are systematic sampling artefacts or errors in the measurements, or we are missing something central in our description of adiabatic droplet activation and growth to establish true closure since the algorithm forces parameter values to the bounds of their observed values to match the measured droplet size distribution. This can be attributed either to a miss-representation of the parameters held fixed during the MCMC simulations, or some droplet growth process(s) being unaccounted for in our pseudo-adiabatic cloud parcel model.

It is shown that the reason for the tendency for the algorithm to head towards unrealistically high values for the geometric standard deviation and mean radius, and low values of the updraft velocity is attributed to forcing

the model to capture the observed width of the droplet size distribution. To ascertain the contribution of this discrepancy from parameter(s) not included or dynamical processes we repeat our simulations, this time including the lognormal parameters describing the Aitken mode, surface tension, and mass accommodation coefficient in the optimisation. This was not found to remove the skew from the median measured values of the aforementioned parameters. Thus in order to achieve closure to cloud droplet size distribution measurements using adiabatic cloud parcel models, it is likely we need to consider additional dynamical processes. It remains for future studies to test the process descriptions by making modifications to our cloud parcel model and repeating the inverse modeling procedure.

5. Discussion and Synthesis

In paper I a new trajectory-driven aerosol and chemical process model is presented and extensively tested. It is shown that nucleation governs the number concentration during transport from clean areas whereas primary emissions dominate the source of particle number for polluted regions in agreement with previous studies (Spracklen et al., 2006). The importance of nucleation for controlling particle number in clean air masses highlights the importance of accurately including this process in GCMs for the accurate prediction of global aerosol concentrations, and subsequent CCN numbers. Moreover, it was shown that switching off nucleation for polluted (continental) cases, resulted in a small change in the resulting size distribution at Hyytiälä, indicating that primary production is the dominant source of particles for these cases. This is an important result in the light of the fact that future aerosol emission scenarios indicate a reduction in the global mean aerosol burden after 2020 (Stier et al., 2006). In a future atmosphere where the anthropogenic burden is less, a shift towards an increase in nucleation events for advection of air from continental environments may be observed.

As CALM has been shown to reproduce the observed aerosol size distribution with respect to growth mechanisms it could be applied also to probe future emission scenarios to improve our understanding of the possible feedbacks associated with a decrease in the anthropogenic aerosol burden and possible increase in aerosols originating from the biosphere. However, whilst CALM has been shown to reproduce the aerosol properties for present day conditions this does not guarantee its success for future atmospheric aerosol conditions. For example, a change in available concentrations of CCN may alter the pathways by which aerosols impact clouds that our simple cloud description in CALM may not accurately capture.

In addition CALM was found to perform less well for winter months, overestimating both the Aitken and accumulation mode number. The cause of this discrepancy is not well understood, but may be linked to more complicated real world winter meteorology which CALM cannot reproduce. The contribution of clouds to this overestimation is difficult to quantify due to the complex feedbacks that govern cloud aerosol interactions. Investigating the role of ice processes which are not included at present in the warm phase cloud parcel model used in CALM is one area for consideration.

As cloud processes in CALM are shown contribute substantially to accumulation mode number it is important to investigate the accuracy of the way cloud processes are treated in more detail. Currently the treatment of droplet activation and in/below cloud scavenging is rather simplified. In summary, to ascertain whether CALM is a robust tool for improving understanding of aerosol evolution and further understand the results presented in paper I it is paramount to assess the accuracy of the treatment of clouds and precipitation in the model. This could be achieved by comparing the performance of the model against aerosol measurements for more receptor sites which are in different aerosol environments, whilst simultaneously comparing against measurements of the cloud microphysical properties.

Without knowing precisely the way clouds act as a sink of aerosol particles it will be difficult to quantify the role of the other processes. It is thus important to study the role of clouds separated from the other processes that alter the aerosol size distribution. Investigating dynamical processes related to cloud-aerosol interactions alone, both in numerical studies and studies performed in combination with observations, provides us with the means to untangle the aforementioned feedbacks. To achieve this papers II-IV concern developing a new inverse modeling framework to investigate cloud-aerosol interactions.

In paper II a response surface analysis was performed to pave the way for an applied use of inverse modelling techniques as a tool to probe cloud-aerosol interactions. It was demonstrated that there is a tipping point between marine and rural continental aerosol environments for the dominating parameters controlling droplet activation; for instance accumulation mode concentration versus chemistry (denoted by the soluble mass fraction) (Figure 8). More research should focus on where this tipping point occurs for a range of different base updraft conditions to help give a clearer picture of global susceptibility.

Building on the experience gained in paper II, in paper III we successfully coupled a pseudo-adiabatic cloud parcel model (Roelofs and Jongen, 2004) to a state of the art MCMC algorithm; DREAM (Vrugt et al., 2008, 2009a). This is an approach that allows us to quantify the global sensitivity of the droplet size distribution towards all model parameters investigated. Strong parameter correlations between multiple model parameters were found that were not evident in our response surface analysis. This suggests that local sensitivity studies and even 2D studies (e.g. Reutter et al., 2009) are have limitations compared to global sensitivity methodologies as they may miss non-linear compensating affects between parameters.

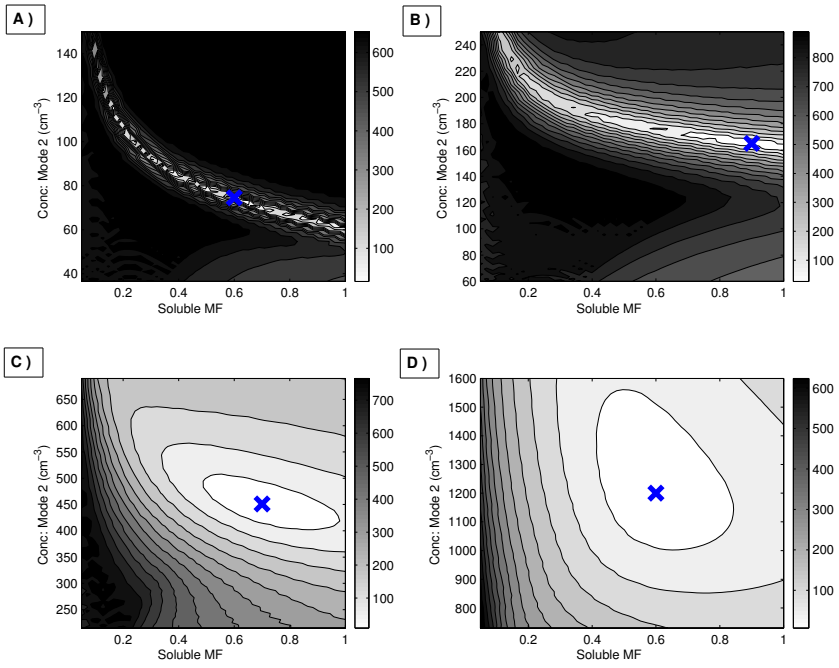

Figure 8: A-D: 2D response surface planes for a selection of two parameter combinations. The blue cross denotes the true parameter values used to generate the synthetic droplet size distribution measurements. Greyscale shows the change in gradient of the OF which provides a measure of droplet size distribution susceptibility: A- Marine Arctic; B- marine average; C- rural continental; D- polluted continental.

By repeating our simulations with variations in the updraft velocity it was shown that the sensitivity to the chemistry increased for lower updrafts, especially in more polluted aerosol environments (Figure 9), corroborating previous studies (e.g. Nenes et al., 2002). The dependence of the sensitivity to chemistry on the base updraft velocity highlights the importance of accurately characterising sub-grid scale variability in this parameter in GCMs.

We also show that the geometric standard deviation can be more important than the mean radius depending on the updraft and aerosol environment (Figure 9). This echoes the results presented by Antilla and Kerminen (2007) who state that the geometric standard deviation can be as important as mean size of mode at low updrafts.

One limitation of this study is that we use seasonal averages of the aerosol physiochemical properties, this being a consequence of the computational time needed for a single MCMC run. We have shown that the parameter sensitivity is highly dependent on the initial conditions, especially the up-

draft velocity. It is therefore important to repeat our approach for shorter timescales and more locations if we wish to get a better picture of the global susceptibility of cloud microphysics to changes in aerosol properties. A further limitation of the results presented in paper III is that some parameters known to be uncertain were not considered. For instance, the relative importance of the surface tension and mass accommodation coefficient were not investigated. Now that the inverse modeling framework for has been established these additional parameters should be investigated as they are known to be highly uncertain (Xue and Feingold, 2004). In addition, to simplify our approach in this first study we do not consider the size dependence of cloud droplet chemical composition. Because the concentration and composition of cloud droplets are not uniform, the transfer of gases onto droplets will depend on the droplet size (Twohy et al., 1989). Model results have shown that use of bulk cloud water parameters such as the soluble mass fraction can lead to substantial errors in the description of processes taking place within individual droplets. Antilla and Kerminen (2007) state that one of the largest sources of uncertainty in their sensitivity conclusions arises from a poor characterisation of the chemical composition and for our study the same applies. A more accurate definition of prior ranges for parameters describing the chemical composition can be used to constrain the PDFs of the corresponding model predictions. This is especially important for this paper in which we use synthetically generated droplet size distributions, as compensation effects between parameters can affect the derived sensitivity. Future inverse modeling investigations must examine more comprehensively the influence of soluble gases, partly soluble material, and surface active materials on water uptake by aerosols and drops.

A final limitation of inverse modeling using synthetically generated cloud droplet size distributions is that we implicitly trust the structure of the pseudo-adiabatic cloud parcel model. However, they can be advantageous for inter-comparing a number of different cloud models/parameterisations and have the potential to highlight how the structural differences between models/parameterisations impact the derived parameter sensitivity in a transparent and detailed way.

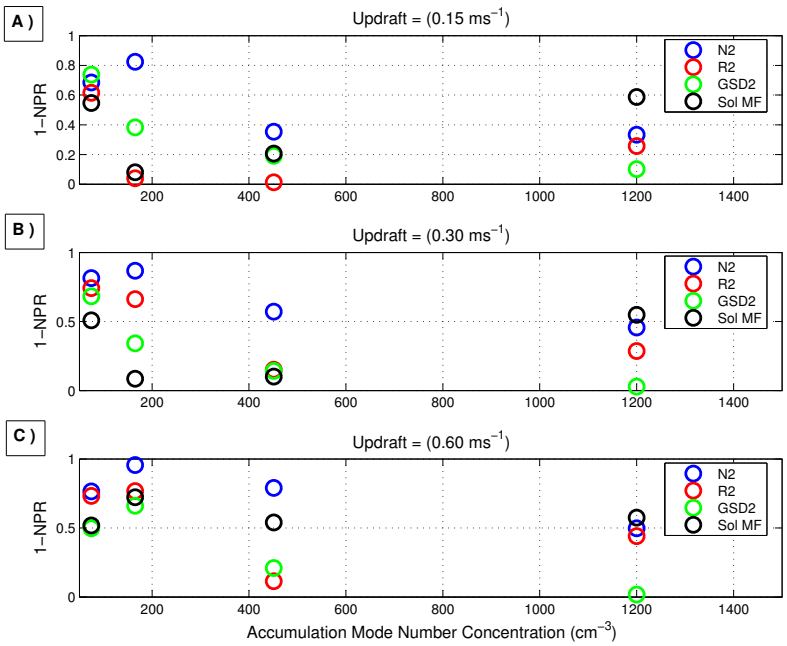

Figure 9: Parameter relative sensitivity for A) Updraft = 0.15 ms^{-1}, B) Updraft = 0.30 ms^{-1}, C) Updraft = 0.60 ms^{-1}. The last 20% of the samples generated with DREAM were used to derive the results. The *y*-axes NPR labels correspond to "Normalized posterior parameter range". Thus, we present the relative sensitivity for the accumulation mode number concentration, mean radius, geometric standard deviation, and soluble mass fraction: N2; R2; GSD2; Sol MF as a function of the accumulation mode number concentration. A higher value of 1-NPR indicates a parameter having higher relative sensitivity. Going from left the light the x- axes corresponds to the accumulation mode number of marine Arctic, marine general, rural continental, and polluted continental conditions respectively.

In paper IV we extend our inverse modelling framework to in-situ observations from the MASE II campaign. The advantage of this over previous closure studies is that it allows us to, in a statistically robust manner; provide a measure of the discrepancy between the simulated and in-situ measurements of cloud droplet size distributions (calibration data) as a function of the aerosol and environmental model input parameters. If the model input parameter values that correspond to the model being optimized to the observed droplet size distribution match their measured counterparts we can have confidence in our process description of droplet activation for Sc clouds.

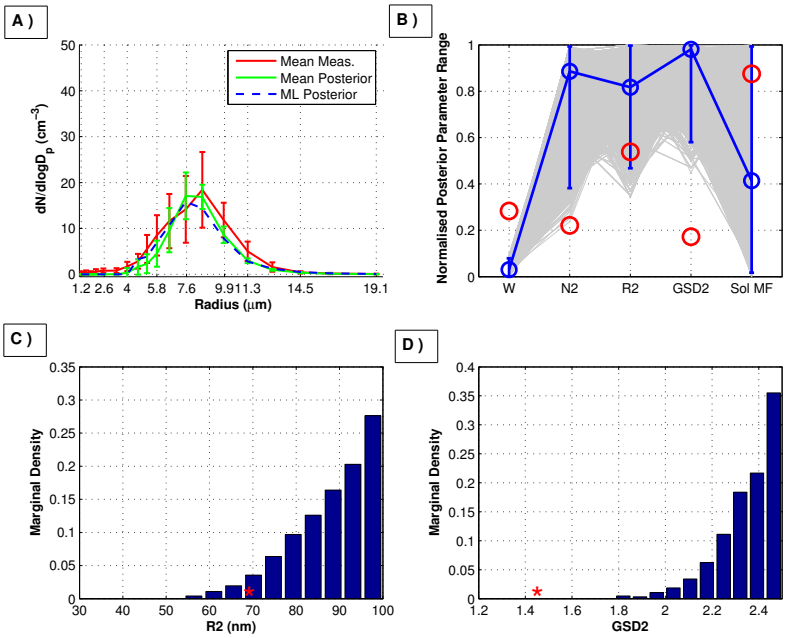

Figure 10: A) The simulated and measured d*N*/dlogD_p droplet size distribution for clean cloud cases RF8. B) The normalized posterior parameter ranges for cloud RF8. The last 20% of the samples generated with DREAM were used to derive the results. The *y*-axes are scaled between 0 and 1 using the prior ranges to yield normalized ranges. A smaller normalized posterior parameter range is indicative of higher sensitivity. The blue error-bars represent define the 1%-99% limits of the posterior distribution. The blue circles are used to signify the maximum likelihood values of the parameters that provide the closest fit (lowest RMSE) to the measured droplet size distribution, whereas the red circles denote the median observed parameter values. Each grey line going from left to right through each panel is a different parameter sample from the posterior distribution. C), D) Histograms of the marginal distributions for the accumulation mode (D_p = 60-120 nm) mean radius and geometric standard deviation. The marginal density provides counts of the parameter values over their posterior distribution range, thus showing the shape of the posterior distribution.

We summarize these main findings for one of the cleaner cloud cases studied (flight number RF8 from MASE II). It is shown in Figure 10a that the optimisation simultaneously shows the closest match to the observed droplet distribution from the optimization procedure and the range in model parameter values required to obtain this match to the observations (Figure 10b).

With regard to the global parameter sensitivity, the modeled droplet size distribution is shown to be more sensitive to changes in lognormal parame-

ters describing the accumulation mode aerosol, in particular those describing its shape and size as compared to chemical composition (Figure 10b). This corroborates the results of previous studies with regard to composition dependence e.g. Dusek et al., 2006. The updraft velocity is the most important parameter which is in agreement with previous modelling and measurement studies. However, during the MASE II campaign, conditions with concentrations of accumulation mode particles (~450 cm^{-3}) were observed for which the aerosol chemistry (represented by the soluble mass fraction) is more important than the accumulation mode (D_p = 60-120 nm) particle concentration. This exception is likely caused by the influence of ship tracks for these particular droplet size distribution measurements, in agreement with the hypothesis posed by Rissman et al., 2004.

However, although the modeled droplet size distribution can be optimized to match the measured droplet size distribution extremely well, probability distributions of the input parameters depart significantly from the median measured values for the mean radius (Figure 10c) and geometric standard deviation (Figure 10d) of the accumulation mode. Thus, the fact that we cannot achieve true closure indicates that we likely miss a dynamical process, parameter(s), or there is a sampling artifact in our measurements. By constraining the geometric standard deviation and repeating our simulations it is demonstrated that the forcing of certain parameters to values that diverge from their respective measured counterparts is due to the algorithm "finding a way" to broaden simulated cloud droplet size distribution in order to match the observations. Effects of the surface tension and mass accommodation efficient are not sufficient to explain the inability of the pseudo-adiabatic cloud parcel model in capturing the broadness of the measured droplet size distribution. The small effects of the mass accommodation coefficient for these marine stratocumulus clouds experiencing low updrafts is in agreement with previous studies (Nenes et al., 2002).

An advantage of the inverse framework used in paper IV is that we very transparently and in high detail highlight that the model may be unsuitable for the measurements which we compare it against. However, the inability to reach true closure (i.e. we do not simultaneously match the calibration data/parameters) can thwart our confidence in derived parameter sensitivity as the inclusion of more dynamical processes necessary to achieve closure may result in a change in balance of the dominating parameters within the cloud parcel model. This highlights the importance of improving our basic understanding of cloud *dynamical* processes before trying to determine sensitivity to aerosol physio-chemical parameters. It was not within the scope of this thesis to pinpoint the cause of discrepancy between measured and simulated aerosol physiochemical parameters.

In order to improve our understanding of which process is missing in our pseudo-adiabatic cloud parcel model, the next step is to repeat our inverse modelling procedure with more processes turned on, such as variable updraft

velocity or with a larger measurement dataset. If the inclusion of additional processes (or process) does not account for the observed deviation from the calibration parameters it would be prudent to repeat our inverse modelling procedure using the same measurements, however with a more complex cloud model. This however poses some difficulties due to the computational demanding nature of MCMC simulations. It is therefore likely that in order to be able to employ a 1D or 2D cloud model it will be necessary to run the DREAM algorithm in parallel using distributed networks to increase the efficiency of MCMC simulation (Vrugt et al., 2006). It should also be noted that our framework is only as good as the measurements with which we have to work with. It would be beneficial to repeat our analysis in paper IV using the coarse mode aerosol properties as optimised parameters, as well as including multiple height levels in the cloud, and also the interstitial aerosol in the calibration data. Entrainment and coalescence are important processes in altering the shape of the cloud droplet number distribution whilst also affecting the partitioning of aerosol between interstitial and cloud droplet (Hallberg et al., 1998). Including the interstitial aerosol in the calibration data may help to discriminate between these various processes and provide more confidence in our understanding of what dynamic processes the pseudo-adiabatic cloud model may be missing.

6. Major Conclusions

In this thesis we have employed two modeling approaches to study aerosol dynamics, and cloud-aerosol interactions.

- The new CALM model is shown to be capable of simulating the most prominent features of the atmospheric aerosol observed at the SMEAR II station. Anthropogenic primary emissions (from the European sub-continent) determine the CN at Hyytiälä when advection from the south occurs. However, when transport of relatively cleaner marine air takes place, the CN is governed by new particle formation. Clouds, as described in CALM, play an important role in regulating especially the accumulation mode concentration. By not considering cloud and precipitation removal, the number of accumulation mode particles is substantially increased.
- Inverse modeling provides a means to ascertain which parameters are the most important for accurately simulating the droplet size distribution, and on the other hand, which parameters are insignificant and potentially can be neglected. Thus, by using inverse modeling we can suggest the type of research efforts required to improve accuracy of simulating cloud microphysical properties.
- To *efficiently* explore the parameter space and calculate the *global sensitivity* of aerosol physiochemical, and meteorological parameters it is necessary to employ statistical tools such as the state-of-the-art MCMC algorithms used in this thesis. The cloud-aerosol inverse problem was found to be extremely difficult to solve for a host of technical reasons as well as significant parameter interactions, multiple regions of attraction, numerous local optima and considerable parameter insensitivity inherent in the system. Despite these issues, both the SCE-UA and DREAM MCMC algorithms were successfully coupled to a pseudo-adiabatic cloud parcel model.
- Local sensitivity analysis and 2D sensitivity analysis have limitations for investigating which aerosol physiochemical properties are the most important for the cloud nucleating ability of a particle, and subsequent simulation of the cloud droplet size distribution due to the strong non-linear interactions between different parameters.
- The updraft velocity is the most important parameter (of those investigated) for controlling droplet activation in liquid phase clouds. The im-

portance of the chemistry (denoted by the soluble mass fraction) is also a strong function of the prevailing updraft. Therefore it is crucial to accurately measure the meteorological properties at cloud base for an accurate assessment of the susceptibility of clouds to perturbations in the aerosol properties. From our results we conclude that the relative importance of the chemistry is a function of the geometric standard deviation of the accumulation mode and therefore it is important to accurately represent in models the width of the accumulation mode for an accurate assessment of the susceptibility of the droplet size distribution to changes in the chemistry.

- It is important to increase our knowledge of the physiochemical properties of the aerosol in clean aerosol environments as the susceptibility of simulated droplet size distributions to variations in aerosol properties is high for cleaner marine and marine arctic aerosol environments. An accurate measurement of the aerosol chemical composition for polluted environments is necessary for the accurate simulation of cloud microphysical properties, especially for low updraft conditions. Using synthetically generated cloud droplet size distributions for an updraft velocity of 0.3 ms^{-1}, a shift towards an increase in the relative importance of chemistry compared to the concentration of accumulation mode number concentration exists somewhere between marine and rural continental aerosol regimes.
- During the MASE II campaign, conditions with concentrations of accumulation mode particles (~450 cm^{-3}) were observed. Marine Sc cloud formation in this region was found to be more sensitive to aerosol chemistry (represented by the soluble mass fraction) than the accumulation mode (D_p = 60-120 nm) particle concentration. Current theory suggests that chemistry can be ignored in all conditions except when an environment is highly polluted. However, our results highlight that under anthropogenic influence, we must also consider chemistry in relatively clean marine environments; *models describing cloud formation should not simply ignore chemical composition*.
- MCMC simulation coupled with a pseudo-adiabatic cloud parcel model can successfully match the observed droplet size distribution for each cloud case for four marine stratocumulus clouds observed during MASE II. In doing so, however, the subsequent agreement between the derived and measured calibration parameters is generally poor. The agreement is especially poor for the updraft velocity, and mean radius/geometric standard deviation of the accumulation mode. Current adiabatic cloud parcel models will in general have difficulty capturing the broadness of measured cloud droplet size distributions for marine Sc clouds. This results in a failure to achieve a full droplet closure between the different model parameters and data. Effects of the surface tension and mass accommodation efficient are not sufficient to explain the inability of the pseudo-

adiabatic cloud parcel model in capturing the broadness of the measured droplet size distribution.

- Our inverse modelling results suggests that the current formulation of the pseudo-adiabatic cloud model is missing a dynamical process rather than parameter(s). Alternatively there may be systematic sampling or averaging artefacts in our observations. Whilst a solution to these problems have not been provided in this thesis, the results still clearly show that inverse modeling provides a comprehensive means to efficiently and in a statistically robust manner test process descriptions in cloud models. Combining the MCMC framework with a number of cloud models and/or parameterisations within models provides a means to guide future research in a more informed manner.

7. Outlook

To understand cloud formation and in particular the aerosol effects on cloud properties it is clear much research is still required. A key gap that we have tried to bridge in this thesis is the synergy between modeling efforts and measurements of cloud and aerosol properties. To achieve this we have embraced MCMC inverse modeling tools in order to investigate the sensitivity of key parameters in the activation of aerosol particles into cloud droplets.

As it has proven useful, I recommend that future studies would benefit from a combination of inverse modeling approaches and in-situ observations, which together will facilitate a transparent assessment of the inadequacies of our cloud model process descriptions. This will contribute to a reduction of the uncertainty in the aerosol indirect effect and allow for increased confidence in climate change predictions.

Measurements

Measurement campaigns of cloud and aerosol properties are inherently expensive and require a great deal of organisational effort. Currently our global database of aerosol properties is sparse, especially in pristine environments. This is problematic as we have shown clouds to be extremely sensitive to aerosol physiochemical perturbations in these environments. Considering these two points, I would like to see the following in future aerosol studies:

- More focus of future measurement campaigns towards areas where currently there is high cloud droplet size distribution susceptibility and currently sparse measurements, e.g. Arctic environment.
- We have shown that aerosol-cloud interactions are highly non-linear and the susceptibility to perturbations in the aerosol physiochemical properties is highly dependent on the prevailing updraft velocity. Thus it is critical when that when investigating cloud-aerosol interactions equal emphasis is placed on both the aerosol and meteorology within the same observation platform.

- I believe it is important to focus measurement campaigns towards improving our understanding of the cloud dynamical processes. For instance by focusing measurements on the properties known to be related to the observed width of the droplet size distribution such as the concentration of giant CCN, and in-cloud turbulence.
- Inverse modeling is only as good as the measurements supplied to perform the inversion, thus I believe it is beneficial to improve the accuracy of certain measured cloud properties known to be uncertain, e.g. the interstitial aerosol.

Modeling

Our current understanding of both the relative importance of aerosol properties for activation and also dynamical processes in clouds is low. Improving our understanding of these parameters and processes will aid in developing accurate yet efficient parameterisations to use in GCMs that can be used to derive improved estimates of aerosol indirect effects. To improve the model representation of the droplet evolution in clouds I propose the following:

- I would like to see future studies that quantify the sensitivity of parameters related to droplet activation use *global sensitivity* methods rather than local sensitivity analysis.
- Many data sets are available of cloud and aerosol properties. The approaches we have developed and presented in this thesis can be efficiently applied to any of these without the inherent costs of starting a new measurement campaign.
- To improve our understanding of how the aerosol controls the cloud microphysics I believe future studies could benefit from performing our inverse modeling framework for both aerosol-CCN closure and aerosol-CDNC closure.
- I believe that repeating the inverse modeling framework presented for a suite of measurements covering a wide range of aerosol-meteorological conditions will aid in eliminating certain processes (or sampling artefacts) as candidates for our inability to reach a full droplet closure. Such efforts will highlight if systematic patterns with respect to the divergence in the model input parameters exist regardless of the environment. This will help ascertain whether we are consistently missing the same process or parameter, and narrow down which it is. However, I believe it is neces-

sary to complement such a strategy with a hierarchy of cloud models to help pin down the weaknesses in our process description.

- Therefore, finally I believe our procedure also lends itself to a process of elimination based approach whereby process representation of droplet size distributions can be improved. This could be achieved by re-using our inverse modeling framework in a stepwise manner by increasing the sophistication of the process description within model (or using models of varying complexity) until a robust closure is obtained. That is, we should find a balance of processes whereby the algorithm does not have to force aerosol or meteorological properties far from measured values to reach closure with droplet measurements. Once this can be achieved consistently for a range of aerosol-meteorological conditions we can be trust the cloud model.

In summary I believe that once our cloud dynamical description is improved, and droplet closure can be obtained it will be much simpler to constrain any remaining parameters which are difficult to measure, thus allowing us to reduce the dimension of number of parameters required in our description of cloud droplet activation with the minimal loss of accuracy. Constraining both structural inaccuracies and parameter uncertainty simultaneously using Bayesian inverse modelling will contribute to the efficient development of cloud parameterisations for GCMs by revealing shortcomings in our process level descriptions.

Appendix – contribution to the papers

Paper I: The original idea to develop a new trajectory driven Lagrangian process model (CALM) using a state of the art description of aerosol dynamical processes originates from Peter Tunved. Peter Tunved developed the CALM model, made the analysis of the model performance, and wrote the paper. The process description of aerosol dry deposition and gas deposition in CALM was performed by Daniel Partridge, as was the model description of these two processes in the paper.

Papers II-IV: The original idea to develop and apply an inverse modeling framework to study cloud-aerosol interactions originates from Daniel Partridge.

Paper II: The data analysis and main investigation was performed by Daniel Partridge. The motivation to calculate response surfaces to investigate the posedness of the inverse problem originates from Jasper Vrugt. The idea to apply response surfaces to provide a graphical illustration of cloud droplet size distribution susceptibility to changes in the updraft and aerosol physiochemical properties originates from Daniel Partridge. Daniel Partridge wrote this paper with input from all co-authors (in particular Jasper Vrugt).

Paper III: Daniel Partridge performed the modeling, data analysis and wrote the paper with input from co-authors. Jasper Vrugt assisted in developing the modeling framework, in particular the development of an appropriate OF for use in the optimization procedure.

Paper IV: Daniel Partridge performed the modeling data analysis and wrote the paper with input from co-authors. Jasper Vrugt helped in developing the model framework, in particular the development of an appropriate OF for use in the optimization procedure. Armin Sorooshian assisted with selecting the flight data.

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Moving to Sweden to begin my PhD studies was the great unknown for me. Little did I know that I would experience the most rewarding, challenging and fascinating period of my life. This time has encapsulated not only forming new lifelong friendships in Scandinavia, but has also led me to travel the world. This chapter of my life is soon coming to a close and although there are elements of regret and relief, I am sure the challenges I have faced and conquered here will have stood me in good stead for the further chapters of the book which are yet to be written. However none of this, or what is yet to come, would be possible without the help and support of family and friends, along with new friends and colleagues, not only here in Sweden but also worldwide.

Firstly I would like to thank my supervisors in Stockholm. Very special thanks to Peter Tunved. How you juggled four young sons at home, a stubborn British PhD student and being there for all my problems I will never know. You and your wife have always treated me as part of your family and even welcomed me into your home at Christmas time. Not only have you been an inspirational scientist but also a great friend. I will always remember celebrating my 25th birthday with you at the research station in Ny-Ålesund 1200Km south of the North Pole.

I also wish to thank Annica Ekman for tirelessly reading my manuscripts and always replying to me in in-human speed – I envy your organisational skills! I am grateful for how supportive you have been of my work over the last few years, the interest you have taken in it and for the encouragement gained from our shared passion for clouds. Now let's do it for ice clouds!

HC Hansen, thank you for allowing me to have so much freedom with my ideas, and running with them even though there were potential risks involved. In addition, my thanks to you for the funding you have been able to provide to facilitate links and collaborations with scientists in other countries. Johan Ström, thank you for sharing your broad knowledge on clouds and aerosols and always helping me to look at problems from a new angle.

My personal aim during this PhD was to try something new that had never been done before in cloud-aerosol research. Finally, sometime into my PhD the nucleus of my idea arrived, and it quickly became apparent to me that there was a requirement to cross over into other scientific disciplines in order for this concept to take shape. This led me to contact Jasper Vrugt. Jasper, this thesis would not have been possible without your agreement to collaborate with me at short notice. When you agreed to join me in this collaboration I'm sure you did not expect it to be so time consuming, or contain so many difficulties. Nevertheless, you have always provided me with immediate support to my questions and problems without any delay or hesitation. This is a special quality, and your approach to scientific research is an inspi-

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And there's one more thing...it's been emotional.

References

Ackerman, A. S., O. B. Toon, J. P. Taylor, D. W. Johnson, P. V. Hobbs, and R. J. Ferek (2000): Effects of aerosols on cloud albedo: Evaluation of Twomey's parameterization of cloud susceptibility using measurements of ship tracks, J Atmos Sci, 57(16), 2684-2695.

Adams, P. J. and Seinfeld, J. H. (2003): Disproportionate impact of particulate emissions on global cloud condensation nuclei concentrations, Geophys. Res. Lett., 30, 1239, doi:10.1029/2002GL016303.

Aitken, J. (1880): On Dusts, Fogs and Clouds, Nature Feb. 384-385.

Albrecht, B. A., (1989): Aerosols, cloud microphysics and fractional cloudiness. Science, 245, 1227–1230.

Andreae, M. O., and Rosenfeld, D. (2008): Aerosol-cloud-precipitation interactions. Part 1. The nature and sources of cloud-active aerosols, Earth Sci. Rev., 89, 13-41.

Anttila, T., and Kerminen, V.-M. (2007): On the contribution of Aitken mode particles to cloud droplet populations at continental rural continental areas – a parametric sensitivity study, Atmos. Chem. Phys., 7, 4625–4637.

Ayers, G. P., and Larson T. V. (1990): Numerical study of droplet size dependent chemistry in oceanic, wintertime, stratus cloud at southern midlattitudes, J. Atmos. Chem., 11(1-2), 143-167.

Birmili, W., Wiedensohler, A., Heintzenberg, J., and Lehmann, K. (2001): Atmospheric particle number size distribution in Central Europe: statistical relations to air masses and meteorology, J. Geophys. Res., 106, 32005-32018, doi:10.1029/2000JD000220.

Boucher, O., and J. Haywood (2001): On summing the components of radiative forcing of climate change, Clim. Dynam., 18(3-4), 297-302.

Bower, K. N., A. Jones, and T. W. Choularton (1999): A modelling study of aerosol processing by stratocumulus clouds and its impact on general circulation model parameterisations of cloud and aerosol, Atmos. Res., 50(3-4), 317-344.

Brechtel, F. J., and S. M. Kreidenweis (2000): Predicting particle critical supersaturation from hygroscopic growth measurements in the humidified TDMA. Part II: Laboratory and ambient studies, J. Atmos. Sci., 57(12), 1872-1887.

Brenguier, J.-L., and W. W. Grabowski (1993): Cumulus entrainment and cloud droplet spectra: A numerical model within a two-dimensional dynamical framework, J. Atmos. Sci., 50, 120–136.

Brenguier, J. L., and Wood, R. (2009): Observational strategies from the micro- to mesoscale, in Clouds in the Perturbed Climate System: There relationship to Energy Balance, Atmospheric Dynamics and Precipitation, edited by J Heintzenberg and R. J. Charlson, pp. 487-510, MIT Press, Cambridge, Mass.

Broekhuizen, K., R. Y. W. Chang, W. R. Leaitch, S. M. Li, and J. P. D. Abbatt (2006): Closure between measured and modeled cloud condensation nuclei (CCN) using size-resolved aerosol compositions in downtown Toronto, Atmos. Chem. Phys., 6, 2513-2524.

Charlson, R. J., J. E. Lovelock, M. O. Andreae, and S. G. Warren (1987): Oceanic Phytoplankton, Atmospheric Sulfur, Cloud Albedo and Climate, Nature, 326(6114), 655-661.

Charlson, R. J., S. E. Schwartz, J. M. Hales, R. D. Cess, J. A. Coakley, J. E. Hansen, and D. J. Hofmann (1992): Climate Forcing by Anthropogenic Aerosols, Science, 255(5043), 423-430.

Chuang, P. Y., R. J. Charlson, and J. H. Seinfeld (1997): Kinetic limitations on droplet formation in clouds, Nature, 390(6660), 594-596.

Chuang, P. Y., D. R. Collins, H. Pawlowska, J. R. Snider, H. H. Jonsson, J. L. Brenguier, R. C. Flagan, and J. H. Seinfeld (2000): CCN measurements during ACE-2 and their relationship to cloud microphysical properties, Tellus B, 52(2), 843-867.

Clark, W. E. and Whitby, K.T. (1967): Concentration and size distribution measurements of atmospheric aerosols and a test of the theory of self-preserving size distributions. J. Atmos. Sci., 24, 677-687.

Conant, W. C., VanReken, T. M., Rissman, T. A., Varutbangkul, V., Jonsson, H. H., Nenes, A., Jimenez, J. L., Delia, A. E., Bahreini, R., Roberts, G. C., Flagan, R. C., and Seinfeld, J. H. (2004): Aerosol, cloud drop concentration closure in warm cumulus, J. Geophys. Res., 109 (D13), doi:10.1029/2003JD004324.

Coulier, P. J. (1875a). Note sur une nouvelle propriete de l'air, J. de Pharmacie et de Chimie, Paris, Ser. 4, 22:165-173.

Coulier, P. J. (1875b). Note sur un nouvelle propriete de l'air, J. de Pharmacie et de Chimie, Paris, Ser. 4, 22:254-255.

Derksen, J. W. B., G. J. H. Roelofs, and T. Rockmann (2009): Influence of entrainment of CCN on microphysical properties of warm cumulus, Atmos. Chem. Phys., 9(16), 6005-6015.

de Reus, M., J. Strom, P. Hoor, J. Lelieveld, and C. Schiller (1999): Particle production in the lowermost stratosphere by convective lifting of the tropopause, J. Geophys. Res., 104(D19), 23935-23940.

Draxler, R. R., and Hess, G. D. (1997): Description of the Hysplit_4 modeling system, NOAA Tech Memo ERL ARL-224.

Duan, Q. Y., S. Sorooshian, and V. Gupta. (1992): Effective and Efficient Global Optimization for Conceptual Rainfall-Runoff Models, Water Resources Research, 28(4), 1015-1031.

Durkee, P. A., et al. (2000): The impact of ship-produced aerosols on the microstructure and albedo of warm marine stratocumulus clouds: A test of MAST hypotheses 1i and 1ii, J. Atmos. Sci., 57(16), 2554-2569.

Dusek, U., D. S. Covert, A. Wiedensohler, C. Neususs, D. Weise, and W. Cantrell (2003): Cloud condensation nuclei spectra derived from size distributions and hygroscopic properties of the aerosol in coastal south-west Portugal during ACE-2, Tellus B, 55(1), 35-53.

Dusek, U., et al. (2006): Size matters more than chemistry for cloud-nucleating ability of aerosol particles, Science, 312(5778), 1375-1378.

Ervens, B., Feingold, G., and Kreidenweis, S. M. (2005): The influence of water-soluble organic carbon on cloud drop number concentration, J. Geophys. Res., 110, D18211.

Ervens, B., M. Cubison, E. Andrews, G. Feingold, J. A. Ogren, J. L. Jimenez, P. DeCarlo, and A. Nenes (2007): Prediction of cloud condensation nucleus number concentration using measurements of aerosol size distributions and composition and light scattering enhancement due to humidity, J. Geophys. Res., 112, D10S32, doi:10.1029/2006JD007426.

Facchini, M. C., M. Mircea, S. Fuzzi, and R. J. Charlson (1999): Cloud albedo enhancement by surface-active organic solutes in growing droplets, Nature, 401(6750), 257-259.

Feingold, G., Cotton, W. R., Kreidenweis, S. M., Stevens, B., (1996): Numerical simulation of stratocumulus processing of cloud condensations nuclei through collision-coalescence, J. Geophys. Res., 101, 21319-21402.

Feingold, G., and P. Y. Chuang (2002): Analysis of the influence of film-forming compounds on droplet growth: Implications for cloud microphysical processes and climate, J. Atmos. Sci., 59(12), 2006-2018.

Feingold, G. (2003): Modeling of the first indirect effect: Analysis of measurement requirements, Geophys. Res. Lett., 30, doi:10.1029/2003GL017967.

Fitzgerald, J. W. (1973): Dependence of the supersaturation spectrum of CCN on aerosol size distribution and composition, J. Atmos. Sci., 30, 628–634.

Fitzgerald, J. W. (1974): Effect of aerosol composition on cloud droplet size distribution - numerical study, J. Atmos. Sci., 31, 1358-1367.

Fountoukis, C., et al. (2007): Aerosol-cloud drop concentration closure for clouds sampled during the International Consortium for Atmospheric Research on Transport and Transformation 2004 campaign, J. Geophys. Res., 112, D10S30, doi:10.1029/2006JD007272.

Gautam, K. K., Tyagi, V. K., (2006): Microbial surfactants: a review. J. Oleo. Sci., 55 (4), 155-166.

Gelfand, A. E., and Smith A. F. (1990): Sampling based approaches to calculating marginal densities, J. Amer. Stat. Assoc., 85, 398-409.

Glantz, P., Noone K.J. and Osborne S.R. (2003): Scavenging efficiencies of aerosol particles in marine stratocumulus clouds. Q. J. R. Meteorol. Soc., 129, 1329-1350.

Hallberg, A., et al. (1997). Microphysics of clouds: Model vs measurements, Atmos. Environ., 31(16), 2453-2462.

Hallberg, A., Noone, K.J. and Ogren, J.A. (1998): Aerosol particles and clouds: Which particles form cloud droplets? Tellus 50B, 59-75.

Hansen, J. E., Sato, M., and Ruedy, R. (1997): Radiative forcing and climate response. J. Geophys. Res., 102, 6831–6864.

Haywood, J., and O. Boucher (2000): Estimates of the direct and indirect radiative forcing due to tropospheric aerosols: A review, Rev. Geophys., 38(4), 513-543.

Hersey, S. P., A. Sorooshian, S. M. Murphy, R. C. Flagan, and J. H. Seinfeld (2009):Aerosol hygroscopicity in the marine atmosphere: A closure study using high-resolution, size-resolved AMS and multiple-RH DASH-SP data, Atmos. Chem. Phys., 9, 2543–2554.

Hegg D.A. and Larson T.V. (1990): The effects of microphysical parameterisation on model predictions of sulfate production in clouds, Tellus, 42B, 272–284.

Heintzenberg, J., D. C. Covert, and Van Dingenen R. (2000): Size distribution and chemical composition of marine aerosols: a compilation and review, Tellus B, 52(4), 1104-1122.

Hoppel, W. A., Frick, G. M., Fitzgerald, J. W., and Larson, R. E. (1994): Marine boundary layer measurements of new particle formation and the effects nonprecipitating clouds have on aerosol size distribution, J. Geophys. Res., 99, 14 443–14 459.

Howard, Luke. The climate of London: Deduced from Meteorological observations. 2 vols. London: W. Philips, 1818-1820 –

Essay on the modification of clouds. London: J. Taylor, 1804.

On the modification of clouds, and on the principles of their production, suspension and destruction. London: J. Taylor, 1804.

Howell, W. E. (1949): The Growth of Cloud Drops in Uniformly Cooled Air, J. Meteorol., 6(2), 134-149.

Hsieh, W. C., Nenes, A., Flagan, R. C., Seinfeld, J. H., Buzorius, G., and H. Jonsson. (2009): Parameterization of cloud droplet size distributions: Comparison with parcel models and observations, J. Geophys. Res., 114, D11205, doi: 10.1029/2008JD011387.

Hudson, J. G., and G. Svensson (1995): Cloud microphysical relationships in California marine stratus, J. Appl. Meteorol., 34, 2655 – 2666, doi:10.1175/1520-0450.

Hudson, J. G., and S. S. Yum (1997): Droplet spectral broadening in marine stratus, J. Atmos. Sci., 54, 2642 – 2654, doi:10.1175/1520- 0469.

Hudson, J. G. (2007): Variability of the relationship between particle size and cloud nucleating ability, Geophys. Res. Lett., 34, L08801, doi: 10.1029/ 2006GL028850.

IPCC (2007): Climate Change: Summary for Policymakers. The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by S. Solomon, D. Qin, M. Manning et al. New York: Cambridge Univ. Press.

Jacobson, M. Z.: Development and application of a new air pollution modeling system-II. Aerosol model structure and design. Atmos. Environ., 31, 131-144, 1997.

Järvinen, H., Räisänen, P., Laine, M., Tamminen, J., Ilin, A., Oja, E., Solonen, A., and Haario, H. (2010): Estimation of ECHAM5 climate model closure parameters with adaptive MCMC, Atmos. Chem. Phys., 10, 9993-10002, doi:10.5194/acp-10-9993-2010.

Junge, C. E. (1969): Comments on "Concentration and size distribution measurements of atmospheric aerosols and a test of the theory of self-preserving size distributions", J. Atmos. Sci., 26, 603-608.

Junge, C. and McLaren, E. (1971): Relationship of cloud nuclei spectra to aerosol size distribution and composition, J. Atmos. Sci., 28, 382–390.

Kaufman, Y. J., I. Koren, L. A. Remer, D. Rosenfeld, and Y. Rudich (2005): The effect of smoke, dust, and pollution aerosol on shallow cloud development over the Atlantic Ocean, P. Natl. Acad. Sci. USA, 102(32), 11207-11212.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J. (2005): Organic aerosol and global climate modeling: a review, Atmos. Chem. Phys., 5, 1053–1123.

Kerminen, V.-M., Pirjola, L., and Kulmala, M. (2001): How significantly does coagulational scavenging limit atmospheric particle production?, J. Geophys. Res., 106, 24119–24126.

Kerminen, V.M., H. Lihavainen, M. Komppula, Y. Viisanen, and M. Kulmala (2005): Direct observational evidence linking atmospheric aerosol formation and cloud droplet activation, Geophys. Res. Lett., 32, L14803, doi:10.1029/2005GL023130.

Koehler, K. A., S. M. Kreidenweis, P. J. DeMott, A. J. Prenni, C. M. Carrico, B. Ervens, and G. Feingold (2006): Water activity and activation diameters from hygroscopicity data - Part II: Application to organic species, Atmos. Chem. Phys., 6, 795-809.

Komppula M., Lihavainen H., Kerminen V.-M., Kulmala M. and Viisanen Y. (2005): Measurements of cloud droplet activation of aerosol particles at a clean

subarctic background site. J. Geophys. Res. 110, D06204, doi:10.1029/2004JD005200.
Korhonen, H., Lehtinen, K. E. J., and Kulmala, M. (2004): Multicomponent aerosol dynamics model UHMA: model development and validation, Atmos. Chem. Phys., 4, 757–771, doi:10.5194/acp-4- 757-2004.
Korhonen, H., Kerminen, V.-M., Lehtinen, K. E. J., and Kulmala, M.: CCN activation and cloud processing in sectional aerosol models with low size resolution. Atmos. Chem. Phys., 5, 2561-2570, 2005.
Kostinski, A. B., and R. A. Shaw, (2005): Fluctuations and luck in droplet growth by coalescence. Bulletin of the American Meteorological Society, 86, 235-244.
Kulmala, M., Hämeri, K., Aalto, P., Mäkelä, J.M., Pirjola, L., Nilsson, E.D., Buzorius, G., Rannik, Ü., Dal Maso, M., Seild, W., Hoffmann, T., Jansson, R., Hansson, H.-C., Viisanen, Y., Laaksonen, A. and O'Dowd, C.D. (2001): Overview of the international project on biogenic aerosol formation in the boreal forest (BIOFOR). Tellus 53 B , pp. 324-343.
Kulmala, M. (2003): How particles nucleate and grow, Science, 302(5647), 1000-1001.
Kulmala, M., et al. (2007): Toward direct measurement of atmospheric nucleation, Science, 318(5847), 89-92.
Köhler, H. (1936): The nucleus in and the growth of hygroscopic droplets. Trans. Faraday Soc. 32:1152–1161.
Laaksonen, A., P. Korhonen, Kulmala, M., and Charlson R. J. (1998): Modification of the Köhler equation to include soluble trace gases and slightly soluble substances, J Atmos Sci, 55(5), 853-862.
Laaksonen, A., Hamed, A., Joutsensaari, J., Hiltunen, L., Cavalli, F., Junkermann, W., Asmi, A., Fuzzi, S., and Facchini, M. C. (2005): Cloud condensation nucleus production from nucleation events at a highly polluted region, Geophys. Res. Lett., 32, L06812, doi:10.1029/2004GL022092.
Lamarck, Jean Baptist (1802): "Sur la forme des nuages" Annuaire. Météorologique pour I'An XI de la République Française, 3,. 149-64, Paris.
Lance, S., Nenes, A., and Rissman T. A. (2004): Chemical and dynamical effects on cloud droplet number: Implications for estimates of the aerosol indirect effect, J. Geophys. Res., 109, D22208, doi: 10.1029/2004JD004596.
Lehtinen, K. E. J., Dal Maso, M., Kulmala, M., and Kerminen, V.- M. (2007): Estimating nucleation rates from apparent particle formation rates and vice versa: Revised formulation of the Kerminen- Kulmala equation, J. Aerosol Sci., 38, 988–994.
Liu, Y. G., and P. H. Daum (2002): Anthropogenic aerosols - Indirect warming effect from dispersion forcing, Nature, 419(6907), 580-581.
Liu, Y. G., P. H. Daum, H. Guo, and Y. R. Peng (2008): Dispersion bias, dispersion effect, and the aerosol-cloud conundrum, , Environ. Res. Lett., 3, 045021.
Lohmann, U., Quaas, J., Kinne, S. and Feichter, J. (2007): Different Approaches for Constraining Global Climate Models of the Anthropogenic Indirect Aerosol Effect. Bull. Amer. Meteorol. Soc., doi:10.1175/BAMS-88–2-243.
Lu, M. L., A. Sorooshian, H. H. Jonsson, G. Feingold, R. C. Flagan, and J. H. Seinfeld (2009): Marine stratocumulus aerosol-cloud relationships in the MASE-II experiment: Precipitation susceptibility in eastern Pacific marine stratocumulus, J. Geophys. Res., 114, D24203, doi:10.1029/2009JD012774.
McFiggans, G., Artaxo, P., Baltensperger, U., et al. (2006): The effect of physical and chemical aerosol properties on warm cloud droplet activation, Atmos. Chem. Phys., 6, 2593–2649.

McNaughton, C. S., Clarke, A. D., Howell, S. G., Moore, K. G., Brekhovskikh, V., Weber, R. J., Orsini, D. A., Covert, D. S., Buzorius, G., Brechtel, F. J., Carmichael, G. R., Tang, Y. H., Eisele, F. L., Mauldin, R. L., Bandy, A. R., Thornton, D. C., and Blomquist, B. (2004): Spatial distribution and size evolution of particles in Asian outflow: Significance of primary and secondary aerosols during ACE-Asia and TRACE-P, J. Geophys. Res., 109, D19S06, doi 10.1029/2003JD003528.

Meskhidze, N., A. Nenes, W. C. Conant, and J. H. Seinfeld (2005): Evaluation of a new cloud droplet activation parameterization with in situ data from CRYSTAL-FACE and CSTRIPE, J. Geophys. Res., 110, D16202, doi:10.1029/2004JD005703.

Metropolis, N., Rosenbluth, A. W., Rosenbluth, M. N., Teller, A. H., and Teller, E. (1953): Equation of state calculations by fast computing machines, J. Chem. Phys., 21, 1087-1092.

Mordy, W. (1959): Computations of the Growth by Condensation of a Population of Cloud Droplets, Tellus, 11(1), 16-44.

Nenes, A., Ghan, S., Abdul-Razzak, H., Chuang, P. Y., Seinfeld, J. H. (2001): Kinetic limitations on cloud droplet formation and impact on cloud albedo, Tellus, 53, 133–149.

Nenes, A., Charlson, R. J., Facchini, M. C., Kulmala, M., Laaksonen, A., and Seinfeld J. H. (2002): Can chemical effects on cloud droplet number rival the first indirect effect?, Geophys. Res. Lett., 29(17), 1848, doi:10.1029/2002GL015295.

Nenes, A., & Seinfeld, J. H. (2003): Parameterization of cloud droplet formation in global climate models. Journal of Geophysical Research, 108(D14), 1-14.

O'Dowd, C.D., Hämeri, K., Mäkelä, J., Väkeva, M., Aalto, P., de Leeuw, G., Kunz, G.J., Becker, E., Hansson, H.C., Allen, A.G., Harrison, R.M., Berresheim, H., Kleefeld, C., Geever, M., Jennings, G. and Kulmala, M. (2002): Coastal New Particle Formation: Environmental Conditions and Aerosol Physicochemical Characteristics During Nucleation Bursts. J. Geophys. Res., 107(D19), 8107, doi:10.1029/2000JD000206.

Pierce, J. R. and Adams, P. J. (2009): Uncertainty in global CCN concentrations from uncertain aerosol nucleation and primary emission rates, Atmos. Chem. Phys., 9, 1339-1356, doi:10.5194/acp-9-1339-2009.

Pinsky, M. B., and A. P. Khain (2002): Effects of in-cloud nucleation and turbulence on droplet spectrum formation in cumulus clouds, Q. J. R. Meteorol. Soc., 128, 501– 533.

Pirjola, L., O'Dowd, C. D., and Kulmala, M. (2002): A model prediction of the yield of cloud condensation nuclei from coastal nucleation events, J. Geophys. Res., 107, 8098, doi:10.1029/2000JD000213.

Platnick, S., and S. Twomey (1994): Determining the susceptibility of cloud albedo to changes in droplet concentration with the Advanced Very High-Resolution Radiometer, J. Appl. Meteorol., 33, 334-347.

Quinn, P. K., Bates, T. S., Coffman, D. J., and Covert, D. S. (2008): Influence of particle size and chemistry on the cloud nucleating properties of aerosols. Atmos. Chem. Phys., 8, 1029–1042.

Radke, L. F., J. A. Coakley, and M. D. King (1989): Direct and Remote-Sensing Observations of the Effects of Ships on Clouds, Science, 246(4934), 1146-1149.

Raes, F., R. Van Dingenen, E. Vignati, J. Wilson, J. P. Putaud, J. H. Seinfeld, and P. Adams (2000): Formation and cycling of aerosols in the global troposphere, Atmos. Environ., 34(25), 4215-4240.

Reutter, P., Su, H., Trentmann, J., Simmel, M., Rose, D., Gunthe, S. S., Wernli, H., Andreae, M. O., and Poschl U.: Aerosol- and updraft-limited regimes of cloud

droplet formation: influence of particle number, size and hygroscopicity on the activation of cloud condensation nuclei (CCN), Atmos. Chem. Phys., 9(18), 7067-7080, 2009.

Rissman, T., Nenes, A., and Seinfeld, J. H. (2004): Chemical amplification (or dampening) of the Twomey effect: Conditions derived from droplet activation theory, J. Atmos. Sci., 61(8), 919–930.

Roelofs, G.J., and Jongen, S. (2004): A model study of the influence of aerosol size and chemical properties on precipitation formation in warm clouds, J. Geophys. Res., 109, D22201, doi:10.1029/2004JD004779.

Roesler, E. L., and J. E. Penner (2010): Can global models ignore the chemical composition of aerosols?, Geophys. Res. Lett., 37, L24809, doi:10.1029/2010GL044282.

Rotstayn, L. D., and Y. G. Liu (2003): Sensitivity of the first indirect aerosol effect to an increase of cloud droplet spectral dispersion with droplet number concentration, J. Climate, 16(21), 3476-3481.

San Martini, F. M. et al. (2006): Implementation of a Markov Chain Monte Carlo method to inorganic aerosol modeling of observations from the MCMA-2003 campaign - Part I: Model description and application to the La Merced site, Atmos. Chem. Phys, 6, 4867-4888.

Shaw, R. A., W. C. Reade, L. R. Collins, and J. Verlinde (1998): Preferential concentration of cloud droplets by turbulence: Effects on the early evolution of cumulus cloud droplet spectra, J. Atmos. Sci., 55, 1965–1976, doi:10.1175/1520-0469.

Singh, H. B., Anderson, B. E., Avery, M. A., Viezee, W., Chen, Y., Tabazadeh, A., Hamill, P., Pueschel, R., Fuelberg, H. E., and Hannan, J. R. (2002): Global distribution and sources of volatile and nonvolatile aerosol in the remote troposphere, J. Geophys. Res., 107, 4121, doi:10.1029/2001JD000486.

Slinn, W. G. N. (1978): Parameterizations for Resuspension and for Wet and Dry Deposition of Particles and Gases for Use in Radiation-Dose Calculations, Nucl. Safety, 19(2), 205-219.

Snider, J. R., and J. L. Brenguier (2000): Cloud condensation nuclei and cloud droplet measurements during ACE-2, Tellus B, 52(2), 828-842.

Snider, J. R., S. Guibert, J. L. Brenguier, and J. P. Putaud (2003): Aerosol activation in marine stratocumulus clouds: 2. Köhler and parcel theory closure studies, J. Geophys. Res., 108, 8629, doi:10.1029/2002JD002692.

Spracklen, D. V., Carslaw, K. S., Kulmala, M., Kerminen, V.-M., Mann, G. W., and Sihto, S.-L. (2006): The contribution of boundary layer nucleation events to total particle concentrations on regional and global scales, Atmos. Chem. Phys., 6, 5631–5648, doi:10.5194/acp-6-5631-2006.

Squires, P., (1956): The microstructure of cumuli in maritime and continental air. Tellus, 8, 443–444.

Srivastava, R. C. (1991): Growth of Cloud Drops by Condensation - Effect of Surface-Tension on the Dispersion of Drop Sizes, J. Atmos. Sci., 48(13), 1596-1605.

Stevens, B., and G. Feingold (2009): Untangling aerosol effects on clouds and precipitation in a buffered system, Nature, 461(7264), 607-613.

Stier, P., Feichter, J., Roeckner, E., Kloster, S., and Esch, M. (2006): The evolution of the global aerosol system in a transient climate simulation from 1860 to 2100, Atmos. Chem. Phys., 6, 3059-3076, doi:10.5194/acp-6-3059-2006.

Stothers, R. B. (1984): The Great Tambora Eruption in 1815 and Its Aftermath, Science, 224(4654), 1191-1198.

Stroud, C. A., et al. (2007): Cloud activating properties of aerosol observed during CELTIC, J. Atmos. Sci., 64(2), 441-459.

Tunved, P., Nilsson, E. D., Hansson, H. C., Strom, J., Kulmala, M., Aalto, P. and Viisanen Y. (2005): Aerosol characteristics of air masses in northern Europe: Influences of location, transport, sinks, and sources, J. Geophys. Res., 110, D07201, doi:10.1029/2004JD005085.

Tunved, P., Hansson, H. C., Kerminen, V. M., Strom, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P. P., Komppula, M., and Kulmala, M. (2006): High natural aerosol loading over boreal forests, Science, 312, 261–263.

Twohy, C.H., Austin, P.H. and Charlson, R.J., (1989): Chemical consequences of the initial diffusional growth of cloud droplets: a clean marine case. Tellus 41B, pp. 51–60.

Twohy, C. H., Clement, C. F., Gandrud, B. W., Weinheimer, A.J., Campos, T. L., Baumgardner, D., Brune, W. H., Faloona, I., Sachse, G. W., Vay, S. A., and Tan, D. (2002): Deep convection as a source of new particles in the midlatitude upper troposphere, J. Geophys. Res., 107, 4560, doi:10.1029/2001JD000323.

Twohy, C. H., and Anderson, J. R. (2008): Droplet nuclei in non-precipitating clouds: composition and size matter, Environ. Res. Letters. 3: doi: 10.1088/1748-9326/3/4/045002.

Twomey, S., (1959): The supersaturation in natural clouds and the variation of cloud droplet concentration. Geofis. Pura. Appl., 43,243–249.

Twomey, S. (1974): Pollution and the planetary albedo, Atmos. Environ., 8, 1251–1256.

Twomey, S. (1977): The influence of pollution on the shortwave albedo of clouds, J. Atmos. Sci., 34, 1149– 1152.

Vrugt, J. A., B. O Nuallain, B. A. Robinson, W. Bouten, S. C. Dekker, and P. M. A. Sloot (2006): Application of parallel computing to stochastic parameter estimation in environmental models, Computers & Geosciences, 32(8), 1139-1155.

Vrugt, J.A., Braak, C. J. F. Ter., Clark, M. P., Hyman, J. M., and Robinson, B. A. (2008): Treatment of input uncertainty in hydrologic modelling: Doing hydrology backward with Markov chain Monte Carlo simulation, Water Resources Research., 44, W00B09, doi: 10.1029/2007WR006720.

Vrugt, J.A., Braak, C. J. F. Ter., Diks, C. G. H., Robinson, B. A., Hyman, J. M., and Higdon, D. (2009a): Accelerating Markov chain Monte Carlo simulation by differential evolution with self-adaptive randomized subspace sampling, International Journal of Nonlinear Sciences and Numerical Simulation., 10, 273 - 290.

Vrugt, J. A., Robinson, B. A., and Hyman, J. M. (2009b): Self-Adaptive Multimethod Search for Global Optimization in Real-Parameter Spaces, IEEE Transactions on Evolutionary Computation, Vol. 13, 2, 243-259.

Wang, J., P. H. Daum, S. S. Yum, Y. A. Liu, G. I. Senum, M. L. Lu, J. H. Seinfeld, and H. Jonsson (2009): Observations of marine stratocumulus microphysics and implications for processes controlling droplet spectra: Results from the Marine Stratus/Stratocumulus Experiment, J. Geophys. Res., 114, D18210, doi:10.1029/2008JD011035.

Warneck, P. (1998): Chemistry of the natural atmosphere, Academic Press.

Warren, S. G., C. J. Hahn, J. London, R. M. Chervine, and R. L. Jenne, (1986a): Global distribution of total cloud cover and cloud type amounts over land. NCAR Tech. Note NCAR/TN-273 STR, 29 pp.

Warren, S. G., C. J. Hahn, J. London, R. M. Chervine, and R. L. Jenne, (1986b): Global distribution of total cloud cover and cloud type amounts over ocean. NCAR Tech. Note NCAR/TN-317 STR, 42 pp.

Wex, H., F. Stratmann, D. Topping, and G. McFiggans (2008): The Kelvin versus the Raoult Term in the Köhler Equation, J. Atmos. Sci., 65(12), 4004-4016.

Whitby, K. (1978): The physical characteristics of sulfur aerosols, Atmos. Environ., 12, 135–159, doi:10.1016/0004-6981(78)90196-8, (reprinted in: Haagen-Smit Prize Special Supplement, Atmos. Environ., 41, S25–S49, doi:10.1016/j.atmosenv.2007.10.057, 2007).

Xue, H., and G. Feingold (2004): A modeling study of the effect of nitric acid on cloud properties. J. Geophys. Res., 109, D18204, doi:10.1029/2004JD004750.

Yum, S. S., and J. G. Hudson (2005): Adiabatic predictions and observations of cloud droplet spectral broadness, Atmos. Res., 73(3-4), 203-223.

Zhang, Y., Seigneur, C., Seinfeld, J. H., Jacobson, M. Z., and Binkowski, F. S.: Simulation of aerosol dynamics: A comparative review of algorithms used in air quality models. Aerosol Sci. Technol., 31, 487-514, 1999.

Zhao, C. S., et al. (2006): Aircraft measurements of cloud droplet spectral dispersion and implications for indirect aerosol radiative forcing, Geophys. Res. Lett., 33, L16809, doi:10.1029/2006GL026653.