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Aerosol-cloud-precipitation interactions. Part 1. The nature and sources of cloud-active aerosols

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ABSTRACT

Atmospheric aerosol particles serve as condensation nuclei for the formation of both, cloud droplets and atmospheric ice particles. As a result, they exert a substantial influence on the microphysical properties of water and ice clouds, which in turn affect the processes that lead to the formation of rain, snow, hail, and other forms of precipitation. In recent years, considerable progress has been made in understanding the chemical composition of aerosols, their microphysical properties, and the factors that enable them to act as cloud condensation nuclei (CCN) and ice nuclei (IN).

The first part of this review article will focus on the nature and sources of CCN and IN. We discuss the fundamentals of the cloud droplet and ice nucleation processes, and the role that the chemical composition and particle size play in this process. We show that, in many instances, the influence of chemical composition can be represented by a simple parameterization, which leaves particle size as the main variable controlling CCN efficiency.

Aerosol particles are produced either directly by anthropogenic and natural sources (dust, sea salt, soot, biological particles, etc.), or they are formed in the atmosphere by condensation of low-volatility compounds (e.g., sulfuric acid or oxidized organic compounds). We discuss the magnitude of these sources, and the CCN and IN characteristics of the particles they produce. In contrast to previous assessments, which focused on the aerosol mass, we are emphasizing the number of particles being produced, as this is the key variable in cloud microphysics. Large uncertainties still exist for many aerosol sources, e.g., the submicron part of the seaspray aerosol, the particles produced by the biosphere, and the secondary organic aerosol. We conclude with a discussion on what particle concentrations may have been in the pristine atmosphere, before the onset on anthropogenic pollution. Model calculations and observations in remote continental regions consistently suggest that CCN concentrations over the pristine continents were similar to those now prevailing over the remote oceans, suggesting that human activities have modified cloud microphysics more than what is reflected in conventional wisdom. The second part of this review will address the effects of changing CCN and IN abundances on precipitation processes, the water cycle, and climate.

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1. Introduction

There is now clear and rapidly growing evidence that atmospheric aerosols have profound impacts on the thermodynamic and radiative energy budgets of the Earth (Houghton et al., 2001; Andreae et al., 2005; IPCC, 2007). Aerosols have a wide range of climate effects that can be broadly classified into direct radiative effects (i.e., those based on the interaction of radiation with the particles themselves), indirect

* Corresponding author. *E-mail address*: andreae@mpch-mainz.mpg.de (M.O. Andreae). effects (i.e., those radiative effects that result from aerosols modifying the abundance and properties of clouds), and other cloud-mediated climatic effects, which act through changing the precipitation processes (Andreae, 1995; Charlson and Heintzenberg, 1995; Lohmann and Feichter, 2005; IPCC, 2007). The growing awareness of the potential climate impacts of anthropogenic aerosols has resulted in a large research effort that has significantly improved our understanding of their role in the Earth's radiative balance. Current understanding of this issue has been summarized in the recent IPCC Assessment (IPCC, 2007), and issues regarding the effects of aerosols on precipitation have been discussed in the report of the World Meteorological Organization International Aerosol Precipitation Science Assessment Group (IAPSAG) (IAPSAG, 2007), a chapter of which has formed the starting point of this review paper (Andreae

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et al., 2007a). The urgency for research in this area has led to the development of a research initiative, *Aerosol, Clouds, Precipitation, and Climate* (ACPC), developed jointly by the IGBP core projects iLEAPS and IGAC, and the WCRP core project GEWEX (Andreae et al., 2007b).

Cloud droplets and ice particles form in the atmosphere by condensation of supersaturated water vapor on aerosol particles. Those particles that have the potential to nucleate liquid cloud droplets are called cloud condensation nuclei (CCN), while aerosol particles that can induce the formation of ice crystals are named ice nuclei (IN). When clouds form in air with elevated concentrations of CCN, they contain higher concentrations of smaller cloud droplets; the resulting reduction in the size of the droplets slows their coalescence into raindrops (e.g., Squires, 1958). This can lead to suppression of precipitation in shallow and short-lived clouds (e.g., Warner, 1968), such as those that form during winter over topographical barriers, and can consequently decrease water resources in semi-arid regions (Rosenfeld et al., 2007a).

When CCN concentrations are low, rain is formed more rapidly, without necessarily the involvement of an ice phase, even in deep convective clouds with warm bases. These clouds prevail in the tropics, as well as during summer in the mid-latitudes. At high CCN concentrations, the "warm" rain formation mechanisms are suppressed due to smaller droplet sizes, and the delay in precipitation can cause the droplets to ascend to supercooled levels (Andreae et al., 2004; Diehl et al., 2007). By not raining early, the condensate can then form ice hydrometeors that release the latent heat of freezing aloft and reabsorb heat at lower levels when they melt. The result is more upward heat transport for the same amount of surface precipitation. The consumption of more static energy for the same amount of precipitation would then be converted to an equally greater amount of released kinetic energy, which could invigorate the convection and lead to greater convective overturning, more precipitation, and deeper depletion of the static instability (Khain et al., 2005; Rosenfeld, 2006).

Another consequence of the suppression of rain formation by aerosol is that atmospheric moisture remains in the atmosphere and is advected downwind, where it can eventually lead to enhanced precipitation at a later time. Thus, at the regional scale, the enhanced and delayed aerosol-induced release of latent heat may lead later to enhancement and re-distribution of convection, low level moisture convergence, and precipitation (Bell et al., 2008).

The reduction in the heating of the Earth's surface due to extinction of solar radiation by aerosols, coupled with direct heating of the atmosphere by elevated absorbing aerosols, may lead to suppression of thermal convection and thereby also reduce rainfall (Koren et al., 2004). It may also produce changes in large scale circulation and moisture transport, which in turn changes cloud, precipitation and aerosol distribution. This amounts to aerosol modulation and interaction with the large scale overturning motions in the tropics and subtropics, such as the monsoons, and the Walker and Hadley circulations, with compensating effects of rain suppression on the downward branch (Bell et al., 2008; Kasahara and Dias, 1986).

Substantial progress has been made in recent years in understanding the source processes that produce cloud-active aerosols, the properties that enable aerosols to act as CCN and IN, the effects of aerosols on cloud physics and precipitation, and the consequences for the climate system. These developments will form the subject of this review. The first part of the review will begin with a discussion of the physical and chemical properties of cloud-active aerosols, focusing on those properties that control droplet and ice crystal activation. This will be followed by a review of the source processes and source strength for the various types of cloud-active aerosols, with emphasis on the number rather than the mass of aerosol particles produced. The paper will close with some thoughts on what the population of cloudactive particles in the atmosphere may have been before it became perturbed by human emissions. In a companion paper we will review the recent progress in the process-based understanding of the interactions between aerosols, clouds, and precipitation (Rosenfeld and Khain, in preparation).

2. Cloud-active aerosols

2.1. Cloud condensation nuclei (CCN) in warm clouds

2.1.1. Fundamentals of cloud droplet activation

In the Earth's atmosphere, cloud droplets or ice particles do not form by homogeneous nucleation of supersaturated water vapor, i.e., condensation of water molecules in the absence of a foreign condensation nucleus. This would require the initial formation of very small droplet embryos with a very small radius of curvature. Fundamental thermodynamics shows that the equilibrium vapor pressure over such a strongly curved surface is much greater than that over a flat surface, the "Kelvin effect". The kinetic theory of homogeneous droplet nucleation predicts that saturation ratios (the actual vapor pressure divided by the equilibrium vapor pressure over a flat surface) of the order of 3.5 to 8 are needed for a cloud of droplets to form by the growth of small clusters of water molecules ("embryos") into droplets (Pruppacher and Klett, 1997; Vehkamäki, 2006). Numerous experimental validations of this theory have been attempted, beginning with Wilson (1900), who found that the saturation ratio in air free of all ions and impurities can reach 8 fold, i.e., reach a relative humidity of 800%, before a cloud of small droplets forms spontaneously in an expansion chamber. The persisting problems in both the theory of homogeneous nucleation as well as in its experimental verification have been summarized by Pruppacher and Klett (1997).

In the real atmosphere, such large supersaturations are never reached, because the presence of aerosol particles greatly facilitates the condensation of water vapor into droplets that grow to diameters of several micrometers to tens of micrometers. This happens because the equilibrium water vapor pressure over a solution is lower than that over pure water (the "Raoult effect"). Water vapor can condense on a soluble aerosol particle, because the Raoult effect opposes the Kelvin effect that results from the small radius of curvature of the nascent droplet. The classical Köhler theory of cloud droplet formation is based on the concept that for each dry soluble particle size there is a "critical supersaturation", S_c , at which the difference between the Raoult and Kelvin effects is at a maximum (Fig. 1). At this point, any infinitesimal increase in the size of the droplet will lead to spontaneous growth into a cloud droplet, since the Kelvin effect decreases with further increase of drop radius. Köhler theory predicts that S_c decreases with increasing size of a soluble particle, or with increasing mass of a soluble substance contained in a mixed particle containing both soluble and insoluble components (Pruppacher and Klett, 1997; Seinfeld and Pandis, 1998).

Insoluble, but wettable particles can also facilitate droplet formation by increasing the radius of curvature of an embryonic droplet that forms on the surface of such a particle, and thereby also opposing the Kelvin effect. The effect is related to the surface free energy of the interface between the particle and the water phase, represented by the contact angle. Hydrophilic substances (i.e., those with low contact angle) strongly facilitate droplet nucleation, whereas hydrophobic substances do not promote droplet formation. Droplet activation by insoluble particles is also influenced by the curvature radius of the surfaces of the particles, and therefore increases with particle size.

Particles that can facilitate the condensation of supersaturated water vapor into cloud droplets under a specified set of conditions are called "cloud condensation nuclei" (CCN). From the preceding discussion it is clear that, whether a particle can act as CCN depends first and foremost on the ambient water vapor supersaturation (S). Thus, the CCN fraction at a given supersaturation (CCN_S) is that subset of the overall aerosol population, which can be activated to cloud droplets at this or a higher supersaturation. Köhler theory predicts that

0.8

this subset is selected based on the amount of soluble matter in the particle. Especially for organic aerosols, however, a series of additional chemical effects can modify the ability of a particle to act as a CCN (Laaksonen et al., 1998; Nenes et al., 2002; Anttila and Kerminen, 2002; Kreidenweis et al., 2006). This issue has been reviewed recently by McFiggans et al. (2006). A summary of the theory and observations regarding the CCN activity of organic aerosol particles has been presented by Sun and Ariya (2006). In the following paragraphs, we will provide a brief overview of these complex phenomena.

Soluble gases, especially nitric acid (HNO₃) ammonia (NH₃), and hydrochloric acid (HCl), can facilitate droplet formation by dissolving in nascent droplets and adding to the solute amount in the droplet (Kulmala et al., 1993; Kulmala et al., 1998; Hegg, 2000; Nenes et al., 2002). Organic compounds in aerosols can influence CCN activity by several mechanisms: contribution of soluble matter, reduction of surface tension, and formation of hydrophobic surface films (Kanakidou et al., 2005). Hydrophilic, soluble organics (e.g., levoglucosan, saccharides, short-chain mono- and dicarboxylic acids) of low molecular weight act essentially the same as inorganic salts, promoting water uptake both in the subsaturated and supersaturated regimes in good agreement with Köhler theory (Peng et al., 2001; Chan et al., 2005; Koehler et al., 2006; Rosenørn et al., 2006). Mixtures of these compounds and inorganic salts show approximately additive behavior, where the organic substances contribute to CCN activity by contributing soluble matter (Abbatt et al., 2005; Mircea et al., 2005; Badger et al., 2006; Svenningsson et al., 2006; Petters and Kreidenweis, 2007). Aerosols made from water soluble organic compounds (WSOC) and humic-like substances (HULIS) extracted from aerosol samples, and aquatic humic and fulvic acids showed similar behavior, with moderate water uptake below 100% RH, and ready droplet nucleation in the supersaturated regime (Gysel et al., 2004; Badger et al., 2006; Svenningsson et al., 2006).

Slightly soluble substances in the aerosol, especially organic compounds, can also add significant solute mass to the aqueous phase of droplets as humidity approaches 100% RH (Shantz et al., 2003; Bilde and Svenningsson, 2004; Hartz et al., 2006). Dissolution of sparingly soluble substances is further facilitated by the presence of metastable liquid residuals that are left behind after a particle has undergone a nucleation/evaporation cycle (Henning et al., 2005; Hartz et al., 2006; Rissman et al., 2007). The fact that aerosols contain a large number of different organic substances implies that, once a liquid phase has formed, it represents a complex multi-component solution with little tendency to re-crystallize upon evaporation (Marcolli et al., 2004).

Finally, a reduction in the surface tension of the droplet, especially due to organic substances, can oppose the Kelvin term and facilitate droplet growth (Facchini et al., 1999; Hitzenberger et al., 2002; Shulman et al., 1996). This effect is reduced, however, when the surfactant molecules partition to the surface of the growing droplet. A recent model study suggests that the surface tension effects of HULIS are important only if they are present at very high weight fractions in the aerosol particles (Kokkola et al., 2006).

At RH below 100%, the uptake of water vapor by particles can also be inhibited by organic compounds, presumably due to the presence of hydrophobic coatings (Saxena and Hildemann, 1996). In the supersaturated regime, this inhibition is overcome, however, and hydrophobic and sparingly soluble substances lead to a delay, rather than an inhibition of droplet nucleation (Hegg et al., 2001; Feingold and Chuang, 2002; Raymond and Pandis, 2002; Raymond and Pandis, 2003; Shantz et al., 2003). Only in extreme cases, such as with particles having a thick coating of stearic acid (a solid at room temperature) or with soot particles containing a high fraction of nonvolatile organics, has suppression of nucleation been observed (Abbatt et al., 2005; Petzold et al., 2005). On the other hand, even substances that do not go into solution, but are wettable, facilitate droplet nucleation because they reduce surface curvature (Abbatt et al., 2005).

It follows from this discussion that CCN are not a fixed, special type of particle, but a highly variable subset of the ambient aerosol population.



droplets of pure water (dotted curve) and for droplets containing various masses of dissolved (NH₄)₂SO₄ (solid curves) vs. diameter of the droplet (Seinfeld and Pandis, 1998). The water vapor supersaturation, $S(X)=(p/p_0-1)100$, where p is the partial pressure of the water vapor and p_0 is the saturated vapor pressure over a plane surface of water at this temperature. In the indicated example, an ambient water vapor S of 0.15% (dashed line) exceeds the critical value for all ammonium sulfate aerosols with dry diameter $\geq 0.1 \mu$ m. These aerosols will therefore activate and grow into cloud droplets, whereas smaller aerosols remain as unactivated haze particles. Droplets below their corresponding equilibrium curve will shrink by evaporation whereas those above will grow by condensation (the indicated droplets correspond, for example, to a dry diameter of 0.05 μ m).

Size, solute content, the presence of surface-active or slightly soluble substances, the wettability and shape of insoluble particles, and the presence of soluble gases all influence whether a particle can act as a CCN at a given supersaturation. Consequently, there is also no particular "source" of CCN — they originate from all the mechanisms that lead to the formation of atmospheric aerosols (Section 2.3).

The continuity of the droplet activation ability of CCN with increasing *S* is reflected in the CCN supersaturation spectra that are a common way of representing CCN measurements (Pruppacher and Klett, 1997; Hudson and Xie, 1999; Roberts et al., 2001; Yum and Hudson, 2001; Hudson and Yum, 2002; Andreae et al., 2004). Fig. 2 shows a compilation of CCN spectra from a variety of marine and continental sites. We see that, as we progress from low to high supersaturations, successively more particles can become activated. The CCN concentration at *S*=1% (CCN_{1%}) is of interest, as *S* rarely exceeds 1% near cloud base, so that CCN_{1%} represents the maximum number of particles that can become activated at cloud base (see discussion below). The shape of the curve reflects the influence of the size distribution of the particles and the size-dependent chemical composition. At a first approximation, it is defined by the relationship between particle number concentration vs. the number of soluble molecules and ions per particle.

2.1.2. The roles of particle size and composition in controlling CCN activity

In the preceding discussion, we have seen that both size and chemical composition influence the ability of particles to act as CCN. Given the bewildering complexity of aerosol composition, especially of the organic fraction, and its variability with time and place, predicting the CCN ability of ambient aerosols from simple



Fig. 2. Cumulative CCN number concentrations from a variety of environments. SCMS is Small Cumulus Microphysics Study on the east coast of Florida in July and August, 1995 (Hudson and Yum, 2001). ASTEX is Atlantic Stratocumulus Transition Experiment in June, 1992 based in the Azores Islands (Hudson and Xie, 1999). ACE 1 was the First Aerosol Characterization Experiment over the Southern Ocean in November and December, 1995 (Hudson et al., 1998). FIRE 1 was the First ISCCP Regional Experiment off the southern California coast in June and July, 1987 (Hudson and Xie, 1999). SHEBA was the Surface Heat Budget of the Arctic Ocean project north of Alaska in May, 1998 (Yum and Hudson, 2001). The colored symbols represent the Amazon Basin during the biomass-burning season (Andreae et al., 2004; Vestin et al., 2007) and during the rainy season (Roberts et al., 2001), and sites outside the cities of Guangzhou and Beijing, China, during summer (D. Rose, unpublished data, 2006). (Figure modified from Hudson and Yum (2002)). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

observations appears to be a hopeless task. To address this issue, we first need to define a property that reflects the ability of aerosol particles from a given population to nucleate cloud droplets. For this purpose, we normalize CCN spectra by dividing the CCN concentration by the total number of particles (CN, condensation nuclei) determined with a CN counter, to eliminate the influences related to transport and dilution. This ratio, CCN/CN ("CCN efficiency", or "CCN fraction"), allows a more meaningful comparison of the intrinsic properties of the aerosol population with respect to droplet nucleation. Then, to separate the effects of size and composition, we look at data obtained with CCN spectrometers that first select a specific particle size, and then subject the resulting monodisperse aerosol population to a range of supersaturations (Frank et al., 2006). Examples of the results are illustrated in Fig. 3, which shows CCN efficiency spectra at S=0.4% as a function of particle diameter for various aerosol types.

We see that for the extreme case of pure sulfate and marine aerosol particles, which are completely soluble, a sharp threshold is present, with practically 100% activation of particles above a certain diameter (ca. 50 nm in this case). For a continental "background" aerosol

representing regional pollution levels, 50% activation is reached at about 70 nm, whereas for the other extreme case, a fresh pyrogenic (i.e., biomass smoke) aerosol, a diameter of ca. 125 nm is required to activate 50% of the particles. Particle size exerts the strongest influence of the ability of particles to act as CCN, since soluble mass changes with the third power of particle diameter, but only linearly with soluble fraction (Dusek et al., 2006). In other words, a very drastic change in composition such as the reduction of soluble fraction from 100% to 10% has about the same effect as a reduction in fully soluble particle size by 50%. The strong dependence of CCN/CN on particle size also explains the wide range observed for this ratio. In aged aerosols, where most particles are in the size range above ~50 nm, the CCN fractions approach 1.0 for S>1% (Hudson and Xie, 1999; Yum and Hudson, 2001; Andreae et al., 2004; Dusek et al., 2006), whereas very low numbers of CCN_{1%}/CN are observed with fresh aerosols that contain a large fraction of particles in the lower Aitken and nucleation size modes.

The relatively weak variability in CCN activity of particles with highly diverse composition (but identical size) becomes less surprising when we consider how this chemical variability is reflected in the soluble content of the aerosols. Comparison of the chemical composition of aerosols from a large variety of sites suggests that the soluble fraction of ambient submicron particles, which provide almost all CCN, varies only over a relatively modest range of about 40-90% (Talbot et al., 1988; Jaenicke, 1988; Liu et al., 1996; Maenhaut et al., 1996; Hegg et al., 1997; Andreae et al., 1999, 2000, 2002; Russell et al., 1999; Zappoli et al., 1999; Quinn et al., 2000; Heintzenberg et al., 2000; Bates et al., 2001; Lelieveld et al., 2001; Ramanathan et al., 2001; Twohy et al., 2001; Artaxo et al., 2002; Clarke et al., 2002; Gabriel et al., 2002; Mayol-Bracero et al., 2002a; Gao et al., 2003; Guyon et al., 2003; Putaud et al., 2004; Gysel et al., 2004; McFiggans et al., 2006; Ervens et al., 2007; Zhang et al., 2007). This factor-of-two range in soluble fraction corresponds to only a 26% difference in diameter. Marine aerosols fall close to the upper bound of this solubility range, whereas some types of fresh biomass smoke or urban particles represent the lower bound. A comparison of continental aerosol compositions in Europe, ranging from curbside to nearly natural sampling environments suggests that in terms of soluble content they are surprisingly similar: about 40±10% inorganic salts, 40±10% organics (half or which are typically watersoluble), with the rest being mineral dust and soot carbon (Fig. 4). One must caution, however, that these bulk composition measurements represent mostly the relatively larger particle sizes, where most of the aerosol mass resides (ca. 0.2-0.8 µm), and that the soluble fraction can be lower in the smallest size classes (<100 nm), especially in urban and near-urban regions (Lehmann et al., 2005). In particular, the organic fraction, which provides fewer solute molecules per unit mass than



Fig. 3. CCN activation spectra at 0.4% supersaturation for different types of aerosols (Frank et al., 2006).

inorganic salts, tends to be enriched in the size class < 100 nm, whereas inorganic salts tend to dominate the soluble fraction in the larger particles (>200 nm) (Broekhuizen et al., 2006; McFiggans et al., 2006). Because these larger particles tend to make up most of the mass of the submicron aerosol, the size-averaged soluble fraction tends to be greater than that in the size range which contains most of the CCN. This leads to a modest overestimation when CCN efficiency is calculated using the size-averaged composition (Medina et al., 2007).

A large number of observations and modeling studies also suggest that, after some atmospheric aging, most particles are at least to some degree internally mixed (Covert and Heintzenberg, 1984; Andreae et al., 1986; Anderson et al., 1996; Middlebrook et al., 1998; Pósfai et al., 1999; Jacobson, 2000; Guazzotti et al., 2001; Okada et al., 2001; Ebert et al., 2002; Lee et al., 2002; Ricard et al., 2002; Weingartner et al., 2002; Allan et al., 2003; Pósfai et al., 2003; Kojima et al., 2004; Hinz et al., 2005; Johnson et al., 2005b; Ervens et al., 2007). This should not be understood in the sense that each particle in a given size class has the same, mixed composition, but that most particles are made up of a variety of soluble and insoluble, organic and inorganic constituents, at somewhat variable proportions. Evidence for this comes from Hygroscopic Tandem Differential Mobility Analyzer (HTDMA) studies and from Aerosol Mass Spectrometer (AMS) measurements, which show that throughout the troposphere almost all particles contain both organics and sulfate (McFiggans et al., 2006; Zhang et al., 2007). Only close to sources, especially in urban air, do we find evidence for the existence of an externally-mixed, combustion-derived component dominated by hydrocarbons and soot particles, which initially shows little or no hygroscopic character. Because SO₂ and NO_x are usually co-emitted with these primary particles, however, condensation of H₂SO₄ and HNO₃ on the initially insoluble particles will quickly add some soluble material (Johnson et al., 2005b). It should be noted that particles can act as CCN even if they contain only quite a small amount (some 5%) of a highly soluble substance, so that particles that may be by some techniques classified as "hydrophobic" and "externally mixed" can still behave as hydrophilic, internally mixed particles in a cloud. A more detailed discussion of these issues can be found in Section 2.3.6.

Consequently, almost all particles contain some deliquescent component that will aid the initial water uptake and growth even of particles dominated by sparingly soluble organic compounds (Bilde and Svenningsson, 2004; McFiggans et al., 2006; Ehn et al., 2007). Such sparingly soluble compounds constitute a significant fraction of the aerosol organic fraction, and appear as insoluble in experiments that determine water uptake under subsaturated conditions (typically up to 80% RH) with an HTDMA, such as those of Lehmann et al. (2005).

On the other hand, they will go into solution at RH>100% and thereby support droplet activation (Cruz and Pandis, 1997; Shantz et al., 2003). The HTDMA measurements therefore represent a lower limit to the soluble fraction relevant to cloud nucleation.

The presence of sparingly soluble and surface-active substances would act to increase the CCN activity of the particles and further reduce the influence of composition on CCN activity because of the counteracting effects of higher molecular weight and reduced surface tension (Ervens et al., 2005). Some allowance must be made for the fact that it is the molar, not the mass concentration of solutes, which determines the magnitude of the Raoult term. Therefore, salts that dissociate into ions of low molecular weight contribute more per unit mass to the number of molecules in solution, and therefore to CCN ability, than organics of higher molecular weights. This is, however, only a minor effect under most circumstances (Corrigan and Novakov, 1999; Ervens et al., 2005). We conclude, therefore, that particle size is the dominant property in controlling the variability in CCN activity (Dusek et al., 2006; McFiggans et al., 2006; Ervens et al., 2007; Pierce et al., 2007), and that the various effects of changing composition (solubility, molecular weight, surface tension, etc.) tend to counteract each other in realistic aerosol mixtures (Ervens et al., 2005). This is most strikingly illustrated by the measurements of Dinar et al. (2006), who measured the CCN ability of aerosols prepared from HULIS that had been extracted from pyrogenic and pollution aerosols. They found that these particles activated at the same or slightly higher diameters than ammonium sulfate particles, and explained this surprising finding with the compensating effects of higher molecular weight and lower surface tension in the HULIS aerosol. The largest deviations of CCN ability at a given particle size from that of particles of "average" composition can be expected when only completely soluble particles are present (e.g., pure sea salt aerosol), or completely insoluble ones (e.g., mineral dust without soluble coatings) (Pierce et al., 2007). At a global scale, however, such conditions are relatively rare, as we discuss in more detail below.

It must be remembered, however, that this analysis mostly refers to "potential" CCN, i.e., those that would nucleate under conditions where nucleation kinetics and competition for water vapor availability do not play a role. Under more realistic conditions, the various "chemical effects" (soluble gases, surfactants, surface films, etc.) may still significantly change the number of droplets that actually nucleate and lead to selective activation of different compositional classes (Kulmala et al., 1996; Nenes et al., 2002; McFiggans et al., 2006). Cloud model calculations that take into account the effect of kinetics and water vapor limitations suggest that sparingly soluble substances behave essentially identically to highly soluble ones, as long as there is at least a small amount of soluble matter present as internal mixture (Abdul-Razzak and



Fig. 4. Aerosol compositions (PM2.5) from a wide range of sampling environments ("natural" to curbside) in Europe (from Putaud et al., 2004).

Ghan, 2005; Ervens et al., 2005). On the other hand, some authors have suggested that the presence of insoluble films may lead to delayed or slower droplet growth, changes in activated fractions, and suppression of activation of specific subsets of the aerosol population (Feingold and Chuang, 2002; Medina and Nenes, 2004; Xue and Feingold, 2004; Petzold et al., 2005). A highly noteworthy result of one modeling study was that surface films could lead to significant broadening of the droplet spectra in clouds (Feingold and Chuang, 2002). Further modeling and experimental studies on this topic are needed.

Field evidence for such differential behavior is scarce. Chuang (2003) observed in Mexico City that a small fraction of particles (0-2%)showed delayed water uptake. Some further evidence comes from studies where the composition of cloud droplets (after re-evaporation) is examined. For example, Sellegri et al. (2003) found that in mountaintop clouds ca. 85% of inorganic ions, but only 14% of organics were present in the cloud droplets, whereas the rest remained in the interstitial aerosol. In contrast, Henning et al. (2002) and Cozic et al. (2007) observed that organic material and soot carbon were scavenged in clouds with about the same efficiency as the overall aerosol, suggesting a high degree of internal mixing and little effect of selective kinetic inhibition. A possible explanation for the differential scavenging observed by Sellegri et al. (2003) could be that the inorganic salts were present in larger particles than the organic material. Overall, these results suggest that for real-world aerosols, away from the immediate vicinity of sources, the effects of limited solubility and surface film formation are likely to be of minor importance.

2.1.3. Parameterization and representation of CCN properties of aerosol particles

In the preceding section, we have shown that the most robust predictors of the ability of a particle to act as CCN are its size and the fraction of soluble matter it contains, i.e., the number of molecules able to go into solution per unit volume of the aerosol material. The soluble fraction can be measured and expressed in a number of different ways (e.g., Fitzgerald, 1973; Fitzgerald et al., 1982; Hudson and Da, 1996; Rissler et al., 2006; Petters and Kreidenweis, 2007). For particles with fully known composition, the number of solute molecules per unit volume can be derived from basic chemical information, and can then be converted to the equivalent number of molecules of a reference solute such as ammonium sulfate (Rissler et al., 2006). The availability of relevant thermodynamic information for many atmospherically relevant substances, especially their dissociation constants and activity coefficients, is, however, limited.

Ambient particles contain a vast number of compounds, especially in the organic fraction, many or most of which are unknown, not individually measurable, and without available thermodynamic information. This makes it impossible to derive a soluble fraction from first principles for such particles. Consequently, empirical techniques have been used to determine the hygroscopicity of ambient aerosols, and water soluble fractions have been derived from these measurements. Broadly, these approaches can be divided into techniques that operate in the subsaturated (RH<100%) and supersaturated (RH>100%) regimes. The most common technique in the subsaturated regime is the Hygroscopic Tandem Differential Mobility Analyzer (HTDMA), which measures the particle growth as a function of RH (Svenningsson et al., 1997; Swietlicki et al., 1999; Busch et al., 2002; Dusek et al., 2003; Rissler et al., 2004; Lehmann et al., 2005; Massling et al., 2005; Mertes et al., 2005; Gasparini et al., 2006; Broekhuizen et al., 2006). The advantage of this technique is that size-resolved hygroscopicity information is obtained, while some alternative techniques, especially the use of nephelometry to determine the increase of light scattering as a function of RH, average over the entire aerosol population (Ervens et al., 2007).

The results of these hygroscopicity measurements have been expressed using a number of related parameters. The soluble volume fraction, ε , can be defined as the volume fraction of a model salt (e.g., $(NH_4)_2SO_4$, NaCl) in a dry particle consisting of the model salt and an

insoluble core, such that the model particle has the same hygroscopic growth as the actual particle. An alternative parameter is κ , defined by Rissler et al. (2006) as the number of soluble moles of ions or nondissociating molecules per unit volume of dry particle. Petters and Kreidenweis (2007) have proposed a related hygroscopicity parameter, coincidentally also named κ , that relates the volume of water taken up by a particle to the water activity. In the following, we will use κ as defined by Petters and Kreidenweis (2007) through its effect on the water activity, a_{w} , of the solution:

$$\frac{1}{a_{\rm w}} = 1 + \kappa \frac{V_{\rm s}}{V_{\rm w}}$$

where $V_{\rm s}$ is the volume of the dry particulate matter and $V_{\rm w}$ is the volume of the water.

In the supersaturated regime, soluble fractions can be obtained from the CCN activation properties of particles with known dry diameter (Fitzgerald and Hoppel, 1982; Hudson and Da, 1996; Dusek et al., 2006). Some authors have expressed the relationship between critical supersaturation and dry diameter using the parameter *B*, which turns out to be almost identical to κ for values of κ >0.2 and S_c <1% (Petters and Kreidenweis, 2007).

Values of κ range from ca. 1.2 for NaCl and 0.6 for (NH₄)₂SO₄ to zero for completely insoluble particles. Laboratory-produced secondary organic aerosol (SOA) and ambient organic aerosols have $\kappa \approx 0.1-0.2$ (VanReken et al., 2005; Prenni et al., 2007) and biomass-burning aerosols range from ca. 0.01 for some very fresh smoke containing mostly soot particles to 0.55 for aerosols from grass burning (M.O. Andreae, unpublished data, 2007; S. Kreidenweis, unpublished data, 2007). The available data from biomass burning suggest that after some short aging, most pyrogenic aerosols will have κ values in the range of 0.1 to 0.3. A summary of k values derived from various sources is presented in Fig. 5. The data plotted in this figure show that continental aerosols fall in a narrow range of κ values around 0.3, consistent with the suggestion by Dusek et al. (2006) that for such aerosols the composition can be treated to a good approximation as invariant, and that the CCN activity of particles is mostly controlled by particle size. In that study, the observed range of κ was 0.15–0.30. While Hudson (2007) correctly points out that field data cover a larger range of B or κ values, his polluted continental data also give an average of κ =0.33±0.15 (average of measurements from Syracuse, NY, Lake Huron, and off California). As expected, his clean marine data (Antigua Island) indicate higher values, with κ =0.87±0.24 (colored bands in Fig. 5). Measurements at the coast of Puerto Rico also showed CCN activation diameters corresponding to κ values in the range 0.6± 0.2 (Allan et al., 2007). A large number of field data has been compiled by Kandler and Schütz (2007), and expressed in the form of soluble fractions, ε . When converted to κ values using the expression $\kappa = \varepsilon \cdot \kappa_m$ (where $\kappa_{\rm m}$ is the κ value of the model salt), these data are also consistent with urban and continental values of κ around 0.2–0.3 and marine values around 0.6. In summary, we propose that for modeling purposes κ values of 0.3±0.1 and 0.7±0.2 can be considered as representative for continental and marine aerosols, respectively.

2.1.4. Giant CCN

Of special interest is the small fraction of particles that can already be activated at very low supersaturations (<0.02%). Fig. 1 shows that these particles must have fairly large dry diameters (>~1 μ m), and they are therefore also referred to as "Giant CCN" (GCCN). Often, GCCN are defined as CCN with dry particle diameters >5 μ m (e.g., Medina and Nenes, 2004). These particles will already grow to quite a large size (>~10 μ m) even before droplet activation, settle at significant speeds, and act as collector drops. At cloudbase, they will be the first to activate, grow readily because of their large surface, and thereby reduce the peak supersaturation in clouds. As a result, they may inhibit the activation of the smaller particles, and therefore play a larger role in shaping cloud

microphysics than suggested by their low number concentrations – usually not more than a few cm⁻³ (Feingold et al., 1999; O'Dowd et al., 1999; Colón-Robles et al., 2006; Hudson and Mishra, 2007). Their rapid growth also enables them to play an important role in precipitation formation under circumstances when high concentrations of pollutant CCN otherwise would suppress warm rain production, such as over polluted ocean regions (Feingold et al., 1999; Yin et al., 2000; Rosenfeld et al., 2002; Rudich et al., 2002; Teller and Levin, 2006; van den Heever et al., 2006), as will be discussed in more detail in the companion paper (Rosenfeld and Khain, in preparation).

The most common source of these giant CCN is the sea spray mechanism over the ocean, where they contribute a few percent to the marine CCN population. Terrestrial sources exist in the form of large ash particles from biomass burning, salt particles from evaporating saline lake basins, and mineral particles containing or coated with sulfates or nitrates (see also Section 2.3.1) (Levin et al., 1996; Rudich et al., 2002; Formenti et al., 2003; Levin et al., 2003). A somewhat unexpected property of these particles is that they often are present in the form of internal mixtures between sea salt, dust, and sulfates (Andreae et al., 1986; Zhang and Iwasaka, 2004; Levin et al., 2005; Zhang et al., 2006). The mechanism by which coagulation of sea salt and dust particles, both present at very low number concentrations, occurs is still unclear. As further discussed in Section 2.3.1, this internal mixing can affect the cloud microphysical behavior of the dust particles. Whereas uncoated dust particles are likely to act as IN only, dust particles that contain soluble material can act as GCCN, and therefore be scavenged before ice nucleation can occur (Levin et al., 2005). A possible further source of GCCN is the emission of very large ash particles from biomass fires. These ash particles contain a large fraction of soluble material, range in size from micrometers to even a few centimeters, and can remain airborne for relatively long times (minutes to hours) because of their low density and convoluted shape (Radke et al., 1991; Andreae et al., 2004).

In contrast to the soluble coatings that enable dust particles to act as GCCN, hydrophobic coatings with film-forming compounds may slow the uptake of water and reduce or eliminate the ability of GCCN to outgrow the rest of the CCN population. Such coatings may originate from the organic materials in the sea-surface microlayer or from anthropogenic pollution. This effect has so far only been demonstrated in model calculations (Medina and Nenes, 2004), and has not been experimentally validated.



Fig. 5. Average relationships between aerosol dry diameter and critical supersaturation. The colored bands reflect polluted continental and clean marine data from Hudson (2007), the colored dots with colored borders are from Dusek et al. (2006) and Andreae (unpublished data), and the colored dots with grey borders have been recalculated from Kandler and Schütz (2007). The lines of constant hygroscopicity, κ , are from Petters and Kreidenweis (2007). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Ice particle nucleation in cold clouds

Ice particles can form in the atmosphere by a multitude of processes (Vali, 1985; Pruppacher and Klett, 1997). In the simplest case, called homogeneous freezing, ice embryos nucleate directly out of the liquid phase without involvement of solid ice nuclei. For supercooled dilute droplets, such as are typically present in deep convective clouds, this occurs at about -36 to -38 °C (Rosenfeld and Woodley, 2000). In the case of liquid aerosol particles with high solute concentrations, e.g., some types of cirrus or polar stratospheric clouds, homogeneous freezing requires even lower temperatures.

Solid, insoluble particles with suitable surface structure can initiate freezing at temperatures well above those typical for homogeneous freezing, and are called ice nuclei. Such particles are rare: typically less than one in a million of atmospheric particles can act as IN. Several heterogeneous freezing mechanisms have been proposed: Immersion freezing occurs when an IN particle immersed in a liquid droplet initiates freezing, whereas contact freezing involves the collision of an IN particle with a liquid droplet. Water vapor condensing on a particle can result either in deposition nucleation, where the ice forms directly as a solid phase upon condensation, or in condensation freezing, where condensation yields an initial liquid phase that subsequently freezes.

Mineral dust particles have been shown to be effective IN in laboratory studies (Roberts and Hallett, 1968; Zuberi et al., 2002; Hung et al., 2003). This can occur by all four of the mechanisms given above; in the case where the dust particles contain soluble material, immersion freezing might be favored. Since such particles can act both as IN and GCCN (see Section 2.1.4), there will be a competition between rapid early growth and sedimentation of these particles as large liquid droplets on one hand, and lofting to the freezing level where they can promote ice formation on the other (Levin et al., 1996, 2005; Teller and Levin, 2006; van den Heever et al., 2006).

Primary biogenic particles, e.g., bacteria, pollen and spores, can also induce ice formation at temperatures well above the range of homogeneous freezing (Vali et al., 1976; Szyrmer and Zawadzki, 1997; Diehl et al., 2001; Möhler et al., 2007). Ice nucleation on soot particles is more complex: whereas relatively pure soot particles appear to be able to induce heterogeneous ice formation from water vapor (albeit at much higher supersaturations than mineral dust), this ability appears to be reduced by the presence of organic materials or sulfuric acid (Demott, 1990; DeMott et al., 1999; Möhler et al., 2005; Dymarska et al., 2006; Kanji and Abbatt, 2006; Kärcher et al., 2007). The latter type of particle first nucleates as a liquid cloud droplet and eventually undergoes homogeneous freezing of the supercooled solution attached to the soot particle. Because soot particles are usually co-emitted with soluble organic carbon and the precursors of sulfate and nitrate aerosol, internal mixing and condensation of soluble inorganics take place fairly rapidly, and bare soot particles are uncommon in even slightly aged airmasses (see further discussion in Section 2.3.6). Consequently, the role of soot particles as IN is probably limited to cirrus formation by homogeneous freezing in the presence of few efficient dust ice nuclei (Kärcher et al., 2007).

Organic matter is generally considered to impede ice nucleation (DeMott et al., 2003a; Cziczo et al., 2004; Kärcher and Koop, 2005), and organic particles in the laboratory have been shown to freeze only at low temperatures by homogeneous freezing (Prenni et al., 2001). However, it was recently proposed that oxalic acid could crystallize from freezing cirrus droplets, remain crystalline after sublimation of the water vapor, and subsequently act as heterogeneous ice nuclei (Zobrist et al., 2006). This mechanism remains to be validated by observations, however.

Studies, in which particles that initiate freezing have been isolated from ambient air and counted, have suggested that IN represent a very small subset of the total aerosol population. Such IN particles are typically present at concentrations of 0.01 cm⁻³ or less, which is orders of magnitude below typical aerosol number concentrations. This exclusivity has bestowed a considerable mystique on ice nuclei,

and a sizeable number of studies have attempted to reveal their identity. The earlier studies exposed aerosol samples on filters to supersaturated water vapor at subfreezing temperatures. More recent work has mostly been carried out by evaporating ice particles collected from clouds using the counterflow virtual impactor (CVI) (Noone et al., 1993; Heintzenberg et al., 1996; Petzold et al., 1998; Seifert et al., 2003; Seifert et al., 2004; Targino et al., 2006). Most of these studies were made in cirrus clouds and consistently found that a large majority (>90%) of ice particle residuals was in the submicron size range (mostly < 100 nm) and that most of these particles (60–90%) were volatile at 250 °C, suggesting that they are made up of sulfates (Seifert et al., 2004). Black carbon (soot) particles were the other dominant component in submicron cirrus residual particles (Petzold et al., 1998; Kärcher et al., 2007). The larger size fractions were dominated by silicate and iron oxide minerals, organic particles and sea salt (Cziczo et al., 2004; Twohy and Poellot, 2005; Targino et al., 2006). It must be noted that this type of study does not differentiate between CCN and IN; any aerosol particle that grew into an ice particle, be it by homogeneous or heterogeneous freezing, is detected by this technique, independent of a specific ability of the aerosol particle to induce freezing. Consequently, the composition of the ice particle residuals sampled at the lowest temperatures (<-35 °C), where homogenous freezing is prevalent, is very similar to what we would expect the CCN population to be (Field et al., 2001). Samples taken at higher temperatures, about -25 to -35 °C, contain more insoluble residual particles, suggesting that heterogeneous freezing has played a more important role (Twohy and Poellot, 2005).

Recently, a number of studies have been published in which ice crystals were nucleated on ambient aerosol particles aboard aircraft or at mountain sites. This technique, the continuous flow diffusion chamber, can isolate those particles that induce heterogeneous ice nucleation. After evaporating the ice, the nuclei were identified by SEM–EDX or an aerosol mass spectrometer. These studies suggest that mineral dust, fly ash, biological particles, some combustion-derived aerosols, as well as metallic particles of meteoritic or technical origin, account for the majority of IN (Rogers et al., 1998; Rogers et al., 2001; DeMott et al., 2003a,b). The number concentrations of these particles were always low (typically <0.001–1 cm⁻³), and reached values of around 1 cm⁻³ only in dust plumes.

In summary, most ice particles in the atmosphere appear to form by homogeneous freezing at temperatures near or below -37 °C, followed by ice multiplication (Hallett and Mossop, 1974; Hobbs and Rangno, 1985). There is, however, a small but cloud microphysically very important fraction of ice particles that are initiated at warmer temperatures by the action of insoluble solid particles with favorable surface properties, the ice nuclei. Mineral dust, primary biogenic particles, and some industrial/combustion-derived anthropogenic particles are the most common IN, and are always found at very low number concentrations relative to the CCN.

2.3. Sources of CCN

To study human impacts on clouds and precipitation, we must be able to contrast natural and anthropogenic aerosol populations, and to quantify natural and anthropogenic sources of CCN. Several assessments of aerosol sources have been made previously (Jaenicke, 1993; Andreae, 1995; Penner et al., 2001; Granier et al., 2004; Andreae et al., 2007a), and most papers describing the role of aerosols in climate models contain an often extensive discussion of aerosol sources. Some of the difficulties with deriving source estimates have been discussed extensively in these papers (e.g., the uncertainties in emission factors and activity estimates, spatial and temporal resolution), and will not be repeated here. Instead, we will highlight some additional issues that must be confronted when attempting to assess CCN sources.

Modeling the role of aerosols in cloud and precipitation processes requires knowledge of the 4-D (space and time) distribution of CCN and IN (at specified *S*). This is a far more demanding task than what has been done in "conventional" aerosol budgets that limited themselves to specifying sources, burdens and sinks in terms of masses of particular aerosol components or "species". Because of the large variability in size distributions, mass and number concentrations of aerosols are not uniquely related. In aerosol–aerosol interactions, masses are additive, while numbers are not. For example, coagulation of particles conserves mass, while number decreases. On the other hand, during condensational growth of particles number remains constant, while mass increases. When we are focusing on the subset of particles that can act as CCN, further complications arise. Coagulation of two particles too small to be CCN may produce one CCN (thereby increasing CCN concentration while decreasing particle concentration), while coagulation of two CCN would also produce one CCN (decreasing CCN concentration and total particle concentration).

Discussion of CCN sources and distributions must take into account that, away from sources, most aerosol particles are internally mixed, at least to some degree. It is this mixture that defines their cloud dropletnucleating ability. For example, if we had one pure H₂SO₄ and one pure adipic acid particle of 100 nm each, only the former would be a CCN at realistic supersaturations (<1%). If we took the same material, and made from it two mixed particles (containing the same mass), we would have two very efficient CCN. For the effects of aerosols on clouds, even relatively small amounts of soluble material in or on otherwise insoluble particles can cause large differences, and the mixing state of the aerosol cannot be ignored. A few mass percent of sulfate in a soot particle can make the difference between it acting as a CCN or not. Fortunately, the usually large degree of internal mixing and the ubiquity of condensational deposition of soluble species on aerosol particles also implies that the extreme cases described above are somewhat hypothetical. Field measurements suggest that in mixed aerosol populations, size is a good predictor of CCN ability (Dusek et al., 2006). This reduces somewhat the burden of complexity that must be represented in CCN source parameterizations (see Section 2.1.3).

Furthermore, the very concept of "source strength" is difficult to define for some aerosol types, since the secondary aerosol species (e.g., sulfates and secondary organics) are not directly emitted, but are formed in the atmosphere from gaseous precursors. For these species, the "source" is a set of atmospheric reactions, not a surface emission process, and therefore the production rate is sensitively dependent on the efficiency of these reactions. Consequently, the source estimates for these aerosols depend strongly on how the source processes are represented in the models, and even on the abundance of other aerosol species (Stier et al., 2006a).

For these reasons, a meaningful analysis of the sources and burdens of cloud-active particles must take the form of a comprehensive atmospheric model that contains emissions of precursor gases and primary aerosol species, and accounts for transport, transformations and sink terms of precursor species as well as the interactions of the various aerosol components. This approach also addresses the conceptual problem that, with few exceptions (e.g., coal fly ash or aerosols from metallurgical operations), there are no uniquely "anthropogenic" particles, and that most ambient particles are mixtures of anthropogenic and natural components. Therefore, the distinction between natural and anthropogenic aerosol populations must be based on a study of the magnitude and distribution of the various natural and anthropogenic processes that lead to aerosol emission, production, and modification. Natural source processes are not always easily distinguished from anthropogenic ones. Vegetation fires, for example, have existed on Earth since the evolution of land plants some 400 million years ago, but at present the vast majority of biomass fires are caused by humans, and therefore pyrogenic aerosols must be considered as mostly anthropogenic. In a similar way, mineral dust aerosols have been mobilized in vast amounts from the Earth's deserts throughout geological history, but the human-caused destabilization of soils in arid and semi-arid regions has clearly increased dust fluxes in many regions.

In order to structure the following discussion of CCN origins and sources, we need to adopt some classification scheme. Aerosol particles are classified in a variety of ways — most commonly by type of origin, by size, and by chemical composition. A very useful classification for our purpose is that of primary vs. secondary particles. Primary particles are those that are released directly as particles into the atmosphere (e.g., dust and sea salt), while secondary particles are the product of the conversion of gaseous precursors into aerosols, e.g., the oxidation of SO₂ to H₂SO₄.

Primary aerosols are very important for CCN budgets, because their emission results in a direct increase of number concentrations of particles. Their emission fluxes and burdens have been summarized in Table 1. Since most of them are also relatively large (>100 nm), they are in a size range where they can act as CCN as long as they contain even a modest soluble fraction. For this reason, they play a pivotal role in the CCN budget and in the cloud-mediated effects of aerosols on climate (Adams and Seinfeld, 2003; Lauer and Hendricks, 2006; Pierce et al., 2007). Secondary aerosol, on the other hand, is mostly formed by the deposition of condensable species, e.g., H₂SO₄ or low-volatility organics, on existing particles. This does not increase particle number, but may increase CCN fraction at a given S. In many cases, however, secondary material is "wasted" as far as CCN activity is concerned, especially when it is condensed on fairly large particles that can already activate at low S. From a comprehensive investigation of the aerosol in the outflow of the Asian continent, Clarke et al. (2004) conclude that primary emissions from combustion (mostly BC) can account for ~85% of the observed accumulation mode number. These observations confirm the important role of primary emissions for the global budget of aerosol particles in terms of number concentrations.

The alternative mechanism for increasing the number of particles in the atmosphere is nucleation from the gas phase (Pierce and Adams, 2007), a process that is still poorly understood despite extensive research over the last decades. In the continental boundary layer, distinctive nucleation events have mostly been observed under conditions when aerosol concentrations are very low and there is therefore little opportunity for condensable species, especially H_2SO_4 , to deposit on pre-existing particles (Kulmala et al., 2004b). Alternatively, nucleation events can occur even in polluted regions, when gaseous H_2SO_4 levels are very high, for example in Beijing (Wehner et al., 2004) or in Pittsburgh (Stanier et al., 2004). In the marine boundary layer, on the other hand, nucleation of new particles is thought to be rare on theoretical grounds (Pirjola et al., 2000), and there is only sparse field evidence for new particle production in this regime (Covert et al., 1992; Andreae et al., 1995; Clarke et al., 1998).

The other major nucleation regime is found in the free troposphere, especially in the detrainment region of clouds, where removal of particles, low temperatures, and high humidity favor nucleation (Twohy et al., 2002; Spracklen et al., 2005a,b; Pierce and Adams, 2007, and references therein). These particles can be mixed down into the boundary layer and support particle concentrations of a few hundred cm⁻³ (Raes, 1995; Spracklen et al., 2005a;b). While freshly nucleated particles are initially too small to be able to act as CCN, they can grow to the necessary size by condensation of H₂SO₄ and low-volatility organics (Lihavainen et al., 2003; Kerminen et al., 2005). On the other hand, in the presence of a substantial concentration of pre-existing particles, their number is reduced by coagulation processes. In the first attempt to provide a model-based estimate of the role of particle nucleation in the global atmosphere, Spracklen et al. (2006) find significant enhancements of particle concentrations especially over remote continental areas downwind of polluted regions. Since their study did not consider the size distribution of these particles, no conclusions regarding the CCN budgets can be drawn, however.

In the following discussion of aerosol and CCN emissions, we will use a classification based on a combination of chemical and sourcetype criteria, and attempt to quantify the natural vs. anthropogenic fraction of the emission fluxes. We will focus on those aspects of aerosol emissions that are most relevant to their role in cloud physics and precipitation formation, and emphasize the more recent literature.

Table 1

Particle emission/production and burdens estimated for the year 2000

	Mass emission			Mass Burden	Number Prod.	Number Burden
	"Best guess"	Min	Max			
		Tg a ⁻¹		Tg	a ⁻¹	
Carbonaceous aerosols						
Primary organic (0-2 μm)	95	40	150	1.2	-	310·10 ²⁴
Biomass burning	54	26	70	-	$7 \cdot 10^{27}$	_
Fossil fuel	4	3	9	-	-	-
Biogenic	35	15	70	0.2	-	_
Black carbon (0–2 μm)	10	8	14	0.1	-	270 · 10 ²⁴
Open burning and biofuel	6	5	7	-	-	-
Fossil fuel	4.5	3	6	-	-	-
Secondary organic	28	2.5	83	0.8	-	-
Biogenic	25	2.5	79	0.7	-	-
Anthropogenic	3.5	0.05	4.0	0.08	-	-
Sulfates	200	107	374	2.8	$2 \cdot 10^{28}$	-
Biogenic	57	28	118	1.2	-	-
Volcanic	21	9	48	0.2	-	-
Anthropogenic	122	69	214	1.4	-	-
Nitrates	18	12	27	0.49	-	-
Industrial dust, etc.	100	40	130	1.1	-	-
Sea salt						
d<1 μm	180	60	500	3.5	$7.4 \cdot 10^{26}$	-
d=1–16 μm	9940	3000	20,000	12	$4.6 \cdot 10^{26}$	-
Total	10,130	3000	20,000	15	$1.2 \cdot 10^{27}$	$27 \cdot 10^{24}$
Mineral (soil) dust						
<1 µm	165	-	-	4.7	$4.1 \cdot 10^{25}$	-
1–2.5 μm	496	-	-	12.5	$9.6 \cdot 10^{25}$	-
2.5–10 μm	992	-	-	6	-	-
Total	1600	1000	2150	18±5	$1.4 \cdot 10^{26}$	$11 \cdot 10^{24}$

Range reflects estimates reported in the literature. The actual range of uncertainty may encompass values both larger and smaller than those reported here. Values are based on the following publications: (Andreae, 1995; Andreae and Merlet, 2001; Guelle et al., 2001; Penner et al., 2001; Gong et al., 2002; Luo et al., 2003; Bond et al., 2004; Liousse et al., 2004; Stier et al., 2005; Ito and Penner, 2005; Junker and Liousse, 2006; Bauer et al., 2007; Henze et al., 2007).

2.3.1. Soil dust

Because of its huge mass emission flux, soil or mineral dust is the most prominent aerosol type in satellite imagery of global aerosol distributions (Kaufman et al., 2002, 2005). But, because most of this dust is in the form of large, but relatively few, supermicron particles, the contribution of mineral dust to the atmospheric CCN burden is more modest. The literature on dust source strength and burden has been reviewed by several groups of authors (Tegen, 2003; Zender et al., 2004; Mahowald et al., 2005). In a recent analysis, Cakmur et al. (2006) used an optimization technique to derive a dust source field that minimized the difference between observations and model predictions and obtained a best estimate of $1500-2600 \text{ Tg a}^{-1}$ for the global flux. The current estimates of global annual source fluxes predicted by the various dust deflation and transport models are in the range of 1000–2600 Tg a^{-1} , which has narrowed somewhat since the reviews of Andreae (1995) and IPCC-TAR (Penner et al., 2001). On the other hand, the range of atmospheric dust burdens predicted by the models, 8-36 Tg, remains still quite large, mostly due to differences in the way deposition processes are treated (Israelevich et al., 2002; Tegen et al., 2002; Werner et al., 2002; Zender et al., 2003; Luo et al., 2003; Miller et al., 2004; Tegen et al., 2004).

The impact of dust aerosols on clouds and precipitation depends on the number concentrations of dust particles that can act as CCN and IN, which in turn is a function of their size distribution and composition, particularly the amount of soluble species they contain. Unfortunately, the current dust models do not contain this information in an adequate way. In fact, there are still major discrepancies in the dust size distributions predicted by the models and those observed by various techniques. Near the dust sources, the dust mass distribution in observations and models peaks at large sizes, 10 μ m or greater. More relevant at the regional and global scales, however, is the size distribution after some atmospheric transport and processing has taken place. In the models, the mass mode is then typically in the range of 1.5–3 μ m, while observations show at least twofold greater sizes, with some internal disagreement between different measurement approaches. Measurements of dust mass median diameter (MMD) by aerodynamic methods give a mean of 4.5±1.3 μ m, in good agreement with the results from optical inversion methods (5±1.5 μ m), but considerably below values obtained by optical counter methods (Reid et al., 2003).

In contrast to the mass size distribution, which is always dominated by the supermicron fraction, the number maximum of the dust size distribution is well below 1 µm diameter. For example, Zender et al. (2003) give a number maximum at 0.6 µm diameter. If particles in this size class were completely made up of insoluble silicate minerals, we would not expect that they could act as CCN at commonly found supersaturations, given the relatively high contact angles between water and silicates (Pruppacher and Klett, 1997). In this case, a substantial fraction of dust particles would remain as interstitial aerosol in convective clouds and reach the middle and upper troposphere, where they can act as IN (DeMott et al., 2003b). The issue is, however, complicated by the fact that dust particles may contain soluble materials either already at the time of emission, e.g., in the form of evaporation residues, or that they may become coated with sulfate, nitrate, chloride, or other soluble salts during atmospheric processing, especially in clouds (Andreae et al., 1986; Talbot et al., 1986; Galy-Lacaux et al., 2001; Yin et al., 2002; Formenti et al., 2003; Trochkine et al., 2003; Kelly et al., 2007; Sullivan et al., 2007a,b). Calcium carbonate particles, common in some arid areas (e.g., the Near East, the Asian deserts, and the China loess plateau), can even be completely converted to calcium nitrate or sulfate (Laskin et al., 2005a,b; Hwang and Ro, 2006). There are also frequent observations of internal mixtures of dust and sea salt in dust plumes and in remote aerosols (Andreae et al., 1986; Zhang and Iwasaka, 2004; Zhang et al., 2006).

In contrast to uncoated dust particles, which are likely to remain interstitial, those coated with soluble materials would actually be among the first to be activated and play a role as giant CCN (Laskin et al., 2005a; Matsuki et al., 2005; Kelly et al., 2007). The observations discussed in the previous paragraphs show that the fluxes and burdens of dust aerosols, and the CCN- and IN-active fractions of this aerosol, depend strongly and interactively on atmospheric processes, especially on their behavior in clouds.

Considerable progress has been made in recent years in defining the geographic distribution of dust source areas, and the mechanisms of dust mobilization. These studies have shown that dust mobilization is not a general feature of arid regions, but is concentrated in areas with particularly strong dust emission potential ("preferential source areas"), in particular dry lake beds in arid areas (Israelevich et al., 2002; Prospero et al., 2002; Tegen et al., 2002; Zender et al., 2003; Todd et al., 2007). These landforms contain a high fraction of clay-size particles and therefore have the potential of releasing a high number fraction of small particles compared to the coarser desert dust particles. As mentioned above, the cloud-nucleating properties of these particles depend on their microphysical and chemical properties: On one hand, uncoated clay particles are efficient ice nuclei. On the other, since the dry lake beds generally contain soluble salt residues from the evaporation of saline lake waters, they might be active as CCN (Formenti et al., 2003).

The strong geographic variability in dust sources reflects the fact that dust deflation requires a specific combination of land surface properties (fine soil texture, low soil moisture, sparse vegetation cover) and climate characteristics (low rainfall, high windspeeds, strong gusts) (Washington and Todd, 2005). This strong spatial variability is also reflected in substantial variability at all time scales, from the last glacial maximum to the anthropogenically influenced present and future (Mahowald et al., 2002; Tegen et al., 2002; Werner et al., 2002; Luo et al., 2003). In contrast to some earlier suggestions, anthropogenic soil disturbance is now thought not to be a major factor in dust mobilization at the global scale (Mahowald et al., 2005), and the contribution of dust from agricultural activities is currently estimated to be <10% (Tegen et al., 2004). The increased dust transport from the Sudano-Sahel region, which was once attributed to human disturbances of the soil cover, is now considered to be mostly related to reduced rainfall in that region (Prospero and Lamb, 2003). Regionally, of course, poor land management can have dramatic consequences for dust mobilization, as was seen in the American "Dust Bowl" of the 1930s.

The dependence of dust production on land cover and climate also implies the existence of strong feedbacks. Atmospheric dust affects precipitation both via radiative transfer and cloud microphysics, resulting in feedbacks through soil moisture on dust emission (Mahowald and Kiehl, 2003). Rosenfeld et al. (2001) have suggested a positive feedback between desert dust, suppressing precipitation, and desertification. Model calculations by Miller et al. (2004) show a complex picture. They suggest that, at the regional scale, increased dust loadings result in more rain in the Sahara, thus producing a negative feedback on regional desertification. At the global scale, however, dust reduces rainfall, thus lengthens the lifetime of aerosols, and increases the burden of dust and other aerosols.

Looking into the future, it must be expected that changes in land cover and climate will affect dust fluxes and burdens in the 21st century. The complexity of feedbacks in the dust/climate/land cover system and the difficulties in making climate predictions at regional scales, however, preclude making reliable estimates at the present state of knowledge. One estimate suggests, for example, that dust fluxes may decrease by 10–60% by 2100, as a result of future land use and climate change (Mahowald and Luo, 2003). In contrast, another study suggests smaller changes (10–25%), and predicts increases or decreases depending on which climate/land cover model is used (Tegen et al., 2004).

2.3.2. Sea salt and sea spray aerosol

Sea salt or sea spray aerosols (SSA) account for the largest mass emission flux of all aerosol types, and rival dust aerosols for the highest mass atmospheric burden (Andreae, 1995; Penner et al., 2001; Andreae et al., 2007a). They consist, as their name suggests, mostly of the inorganic salts present in seawater, but also contain a significant amount of organic materials, therefore the term "sea spray aerosol" may be better than "sea salt aerosol". Sea spray aerosol is a component of, but not identical with, the "marine aerosol", i.e., the aerosol in the marine boundary layer, which also contains other particle types, such as sulfates from biogenic and anthropogenic sources, etc.

The presence of organic matter in SSA was reported quite early (Blanchard, 1964), but has received increasing attention in recent years. Several studies in the last few years have shown that SSA contains a substantial amount of organic matter, consisting both of insoluble material (biological debris, microbes, etc.) and water soluble constituents (Novakov et al., 1997; Middlebrook et al., 1998; Cavalli et al., 2004; O'Dowd et al., 2004; Kaku et al., 2006). The fraction of organic components increases with decreasing particle size, and, in biologically active regions, may approach 90% in the size fraction around 100 nm (Cavalli et al., 2004; O'Dowd et al., 2004; Keene et al., 2007; Nilsson et al., 2007). The chemical and isotopic composition of this organic matter suggests a marine biogenic source (Turekian et al., 2003). The extreme case, where organic particles with little or no sea salt are produced from the sea surface will be discussed in the section on primary biogenic aerosols (Section 2.3.3). Organic materials and sea salt are present as internal mixtures, consistent with a production mechanism that involves fragmentation of organic-rich surface film layers during the bursting of air bubbles at the sea surface. Some

evidence from dry particles suggests that the organics may be present as coatings on the surface of salt crystals (Tervahattu et al., 2002). This finding is consistent with the surface-active character of the organics, which was reported by Blanchard (1964), and confirmed in recent studies (Cavalli et al., 2004).

Sea spray particles span a wide size range (ca. 0.05–10 µm diameter), with most of their mass in the supermicron range. Number size distribution measurements available up to 2004 have been compiled by Lewis and Schwartz (2004), and show consistently that the highest number concentration of sea salt particles is in the submicron range, with a pronounced number mode at 200–500 nm dry diameter, and that significant number concentrations are still present at 100 nm. Unfortunately, most field observations to date of sea salt particles only reach down to ca. 100 nm (Gras and Ayers, 1983; O'Dowd et al., 1997; Murphy et al., 1998a; Campuzano-Jost et al., 2003). They typically suggest a rapid drop in SSA number concentrations below this size. This is supported by electron microscopic investigations by Bigg et al. (1995), who found that the smallest identifiable salt particles had a diameter of about 80 nm, but that there were very few such particles below 100 nm.

Recent studies suggest that even smaller particles may actually be the most numerous fraction of the SSA. Evidence for the production of very small sea spray particles comes from laboratory studies by Mårtensson et al. (2003), which indicate that the maximum of the number distribution is actually somewhat below 100 nm (~50-80 nm). In experiments with a large sea spray generator using continuously flowing, fresh seawater, Keene et al. (2007) observed a number mode at 130 nm wet diameter (82% RH), with large amounts of particles still present down to 50 nm. At 33% RH, the modal diameter decreased to ~80 nm. Measurements of sea spray aerosol fluxes at Mace Head showed that roughly equal amounts of particles were produced in the size range 10–100 nm as in the range >100 nm (Geever et al., 2005). Other studies also suggested significant particle production below 100 nm, but did not show a distinct size mode in this range (Nilsson et al., 2001, 2007; Lewis and Schwartz, 2004). Most studies suggest that the majority of sea spray particles smaller than 100 nm consist of organic material with only a small amount of mineral salts (Bigg et al., 1995; Keene et al., 2007; Nilsson et al., 2007). These particles will be discussed in more detail in Section 2.3.3 on primary biogenic aerosols.

The common view that the size distribution of sea salt particles is limited to the range above ~90 nm has, however, been challenged by Clarke et al. (2003, 2006) who found very small sea salt particles, with a number maximum around 30–40 nm, produced by coastal breaking waves. The particles were identified as sea salt by their thermally refractory nature and by the fact that their water uptake as a function of humidity is very similar to that of NaCl.

A substantial source of such very small sea salt or sea spray particles could be of importance to the marine CCN budget, even if they, as originally produced, are below the critical diameter for droplet activation at the low supersaturations found in marine stratus. Such particles could serve as nuclei for the growth of sulfate particles from the oxidation of marine biogenic DMS, providing an alternative mechanism to homogeneous nucleation of sulfate particles, which is thought to be only rarely possible in the clean marine atmosphere (Pirjola et al., 2000; Clarke et al., 2006; Pierce and Adams, 2006).

The dominant production mechanisms for SSA are the bursting of rising air bubbles that have been injected below the sea surface by breaking waves, and the tearing of droplets from wave crests (Lewis and Schwartz, 2004; Schulz et al., 2004). The rates of particle production by both mechanisms are strongly dependent on wind speed, with production of spume droplets from wave tops occurring only at wind speeds >9 m s⁻¹. Under moderate wind regimes, sea spray particle number concentrations are typically about 10 cm⁻³ or less, while under high wind conditions (>10 m s⁻¹), their concentration can rise to 50 cm⁻³ or more (Hoppel and Frick, 1990; O'Dowd et

al., 1997; Shinozuka et al., 2004). Quantitative relationships between wind speed and SSA abundance, however, remain highly uncertain (Lewis and Schwartz, 2004). Boundary layer stability and the presence of surface-active materials also can have a strong influence on SSA production rates.

Estimates of the total sea salt flux from ocean to atmosphere vary over a huge range: 300-30,000 Tg a⁻¹ (Lewis and Schwartz, 2004). Even the most recent estimates show considerable disagreement: Lewis and Schwartz (2004) propose a production rate of 5000 Tg a⁻¹ with a stated uncertainty of a factor of 4, while Schulz et al. (2004) estimates a flux of 19,800 Tg a^{-1} , which is composed of 2690 Tg a^{-1} in a mode centered at 2 μ m diameter and 17,100 Tg a⁻¹ in a mode at 11 μ m diameter. A large part of the differences among these and earlier estimates, however, can be attributed to the choice of the upper size cutoff. With increasing cutoff size, a large mass flux of very coarse and therefore very short-lived salt particles is included in the estimate. It can be argued that these short-lived particles are of little geophysical relevance, and are therefore better not included in flux estimates. For this reason, Lewis and Schwartz (2004) have suggested to adopt the "effective SSA production flux", i.e., the flux that passes through a reference plane at a height of 10 m above the sea surface, as the appropriate metric for SSA production.

For the purposes of our discussion of aerosol-cloud interactions, these estimates of aerosol mass emission are not very helpful, anyway, because most of this SSA mass is in the coarse mode, which contributes only a small fraction of the cloud-active particles. Yet, while their number concentration is low, these large particles may play an important role as GCCN (see Section 2.1.3). On the other hand, the majority of sea spray CCN are in the submicron mode, which accounts for only a minor fraction of the mass (order of 1%). Given that the removal rates and mechanisms, and thus the lifetimes and transport scales are very different for the different size fractions, a meaningful analysis of SSA fluxes, burdens, and atmospheric distributions requires a size-resolved model that includes production, transport, and deposition.

The available parameterizations for the windspeed-dependent, size-resolved emission flux of particles from the sea surface have been summarized by Schulz et al. (2004) and analyzed in detail by Lewis and Schwartz (2004). They conclude that the best match with the observed size distributions (O'Dowd et al., 1997) is obtained using the Gong-Monahan and Vignati schemes (Vignati et al., 2001; Gong, 2003), among which the Gong-Monahan scheme probably has the more faithful representation of the wind-speed dependence. It must be emphasized, however, that the extrapolation from the size range of 0.8-8 µm originally given by Monahan to that required for CCN budgets (well below 100 nm) introduces very large uncertainties (at least an order of magnitude). In contrast, the recent SSA flux study by Nilsson et al. (2007) suggests better agreement with the Mårtensson et al. (2003) parameterization scheme. Comparison between model predictions of SSA mass with observations at individual stations gives little confidence in the skill of present models of SSA production (Lewis and Schwartz, 2004). The estimate used in this paper (Table 1), which was retrieved from the model runs that formed the basis of Stier et al. (2006a), must be seen with these caveats in mind.

There is considerable discussion in the literature about what fraction of the CCN in the marine atmosphere is contributed by SSA. Ideally, this could be addressed by simultaneous measurements of SSA and CCN number concentrations, but unfortunately, such measurements are rare. In one such study, Hobbs (1971) found that the concentrations of sodium-containing particles (SCP) over the ocean decreased sharply with increasing height. However, even at altitudes as low as ~17 m above the ocean surface, and over surf, the concentrations of SCP were only a few percent of the total concentration of CCN at 0.5% supersaturation. Also, the average concentration of CCN did not change significantly with altitude up to at least 3330 m.

Lacking a broad database of simultaneous SSA and CCN measurements, we can compare typical SSA number concentrations $(1-30 \text{ cm}^{-3})$ as compiled from the literature by Lewis and Schwartz (2004) with typical remote marine aerosol number concentrations in the CCN size range (100–500 cm⁻³) (Heintzenberg et al., 2000). These numbers suggest that, in general, sea salt particles are not a major contributor to the CCN population. Under particular circumstances, however, at times and in ocean regions where wind speeds are high and/or other aerosol sources are weak (such as the winter-time remote oceans of the Southern Hemisphere) sea salt may be the dominant contributor to CCN (O'Dowd and Smith, 1993; Quinn et al., 1998; Murphy et al., 1998a; Yoon and Brimblecombe, 2002; Shinozuka et al., 2004; Pierce and Adams, 2006). Sea salt CCN (at 0.5% S) may reach concentrations of the order of $80-100 \text{ cm}^{-3}$ at high windspeeds (17–32 m s⁻¹) (Bigg et al., 1995; Jennings et al., 1998).

The relative importance of SSA particles may be amplified under some circumstances, because the presence of large amounts of SSA can reduce the formation of CCN from the oxidation of DMS by acting as a sink for gaseous H_2SO_4 molecules, thereby reducing the amount of sulfate available for the formation of accumulation mode particles (Andreae et al., 1999; Yoon and Brimblecombe, 2002; Gong and Barrie, 2003). More detailed studies on the size distribution, composition, and production rates of the submicron marine aerosol will be required to resolve these issues.

2.3.3. Primary biogenic aerosols

The term Primary Biogenic Aerosol Particles (PBAP) covers a wide range of particle sizes, compositions, and structures, and includes entire organisms (bacteria, fungi, viruses) as well as debris (Després et al., 2007; Möhler et al., 2007). Although PBAP have been studied for a long time, including by people as famous as Charles Lindbergh (Meier, 1935), they remain poorly understood and their importance underappreciated (Jaenicke, 2005). Their source mechanisms are diverse, often poorly understood, and hard to quantify. Plants shed pollen, as well as various types of debris (cuticular waxes, leaf fragments, etc.), and soil dust contains a mixture of humic matter, plant decomposition products, fungi and microbes. Fungi release spores by a variety of mechanisms, including high-speed catapult-like ejection (Elbert et al., 2007). This release is often predominantly nocturnal, leading to strong diel variability (Graham et al., 2003a; Gilbert, 2005). Certain types of insects produce brochosomes, spherical particles with diameters of a few 100 nm, which are ubiquitously found in the atmosphere (Bigg, 2003). Some types of pollen are also forcibly ejected, usually during daytime (Edwards et al., 2005). Pollen grains may rupture upon moistening, and produce a large number of fragments in the size range 30 nm to 4 µm (Taylor et al., 2002; Taylor and Jonsson, 2004).

As a result of these diverse source processes, PBAP cover a wide size range from tens of microns down to a few tens of nanometers. Morphological studies using light and electron microscopy have shown that PBAP make up a large fraction of the aerosol down to \sim 0.2 μ m at a variety of clean and polluted sites (e.g., the Amazon, Siberia, and even urban Central Europe (Matthias-Maser and Jaenicke, 1995; Matthias-Maser et al., 2000; Graham et al., 2003a,b; Posfai et al., 2003)). The number concentrations of positively identified PBAP are in the range of tens to hundreds per cm³, but the true concentrations could be considerably larger since it becomes quite difficult to unequivocally identify particles in the submicron range as being primary biogenic. Studies over the rainforest have shown the majority of particles to consist of organic matter, but most of them have little or no diagnostic morphological or bulk chemical signatures (Artaxo et al., 1990; Andreae and Crutzen, 1997; Krejci et al., 2005). Chemical tracer studies suggest, however, that primary biogenic material contributes a large fraction of the pristine aerosol even in the submicron size range (Simoneit et al., 1990; Artaxo and Hansson, 1995; Graham et al., 2003b; Guyon et al., 2003, 2004).

Some of the most intriguing PBAP are a variety of particles produced at the sea surface, which consist of mixtures of microorganisms and exopolymer secretions (Leck et al., 2002, 2004; Leck and Bigg, 2005a,b). Current evidence suggests that these particles are released during bubble bursting, similarly to sea salt aerosols (Blanchard, 1983; Aller et al., 2005), but they often contain little or no inorganic salt components. They tend to be most abundant in the Aitken and accumulation modes, and contain a significant fraction of surface-active substances. These particles may enhance the number concentration of primary marine CCN significantly above the value accounted for by sea salt particles (Lohmann and Leck, 2005). Furthermore, small marine PBAP (20–50 nm) may also play a role as growth nuclei for CCN-sized particles over the remote oceans, through condensational growth by deposition of sulfate derived from the oxidation of DMS (Leck and Bigg, 2005a).

There is substantial evidence that PBAP may be able to act both as CCN and IN (Schnell and Vali, 1976; Vali et al., 1976; Levin and Yankofsky, 1983; Franc and DeMott, 1998; Diehl et al., 2001; Sattler et al., 2001; Bauer et al., 2003; Möhler et al., 2007). This is consistent with their often relatively large size and soluble matter content, but their surface properties are also thought to play a significant role (Bauer et al., 2003). It is therefore likely that PBAP represent a significant fraction of CCN and IN in the clean atmosphere, and are therefore of importance for the regulation of cloud microphysical properties under pristine or remote conditions. This is supported by the nearly ubiquitous presence of biological materials in cloud water, rain and snow samples (Amato et al., 2005; Bauer et al., 2002), but not enough is known at this time to assess their role with any confidence.

Since many of these PBAP are of large size and have low water contact angles (Sharma and Rao, 2002), they can be activated already at very low supersaturations (<0.02%) and act as GCCN. Therefore, they will be the first to activate at cloudbase, and can grow readily because of their large surface area. This enables them to play an important role in precipitation formation under circumstances when high concentrations of pollutant CCN otherwise would suppress warm rain production (Yin et al., 2000; Rosenfeld et al., 2002; Rudich et al., 2002).

To date, there are no reliable estimates on the rates of PBAP emissions. The estimates given in Table 1 have been calculated based on the commonly observed mass concentrations of $1-2 \ \mu g \ m^{-3}$ over remote, vegetated continental regions and an estimated atmospheric lifetime of 2 days for these particles, most of which are relatively large and therefore have a fairly high deposition velocity. Since they may play a large role in cloud microphysics in the pristine atmosphere, and because their atmospheric abundance may undergo large changes as a result of land use change, they highly deserve more scientific study.

2.3.4. Secondary organic aerosols

Secondary organic aerosols (SOA) originate from the condensation of organic vapors in the atmosphere. Their precursor compounds may be of biogenic (e.g., terpenes, isoprene) or anthropogenic origin (e.g., petroleum, combustion), but there is general agreement that biogenic precursors are dominant (Griffin et al., 1999a; Chung and Seinfeld, 2002; Derwent et al., 2003; Kanakidou et al., 2005; Tsigaridis et al., 2005; Dentener et al., 2006; Fuzzi et al., 2006). Isoprene in particular, which until the seminal paper by Claeys et al. (2004a) was not considered to contribute to SOA production at all, is now thought to account for almost half of the global SOA formation (Henze et al., 2007).

The important role of biogenic precursors is supported by radiocarbon studies, which show that isotopically "modern" carbon accounts for the largest fraction of OC even in many urban regions (Lewis et al., 2004; Szidat et al., 2004). Production from biogenic precursors does not mean, however, that the resulting SOA concentrations are necessarily "natural", since both the rate of oxidation of biogenic precursors and the transfer of the oxidation products to the condensed phase are enhanced by anthropogenic pollution (Kanakidou et al., 2000).

Atmospheric chemical processes lead to the formation of organic compounds with reduced volatility, which can condense to aerosol particles (Seinfeld and Pankow, 2003). In principle, this could occur by homogeneous nucleation, but there are no actual observations of direct nucleation of SOA particles in the ambient atmosphere. Field and laboratory studies have shown that SOA-rich particles form by condensation of organic gases with low vapor pressures onto preexisting particles, e.g., freshly nucleated sulfate particles in the ultrafine size class, which may be as small as 2–9 nm (Kerminen et al., 2000; Kulmala et al., 2000; Kerminen, 2001; Gao et al., 2001; O'Dowd et al., 2002; Lihavainen et al., 2003; Maria et al., 2004; Zhang et al., 2004a,b; Kulmala et al., 2007a,b). As a result of the small size and mass of these initial sulfate nuclei (Kulmala et al., 2004a; Boy et al., 2006), the resulting SOA particle consists to a large extent of organic material. Still, the small amounts of H_2SO_4 incorporated during nucleation and growth of the SOA particles are enough to substantially enhance their hygroscopicity, especially for the smaller size classes (10–20 nm) (Ehn et al., 2007).

In the presence of high concentrations of SO_2 and a high rate of H_2SO_4 production, new particle formation and growth by incorporation of organics occurs even at a high concentration of pre-existing aerosols, such as found in the cities of Milan and Pittsburg (Baltensperger et al., 2002; Zhang et al., 2004a). In contrast, in clean environments where significant amounts of primary biogenic and other particles act as an efficient sink for condensable organics and the small amounts of gaseous H_2SO_4 produced from biogenic sulfur emissions, nucleation is suppressed and SOA formation proceeds by condensation only. This is most likely the case in environments such as the Amazon Basin, where nucleation events have never been observed, in spite of high concentrations of VOC and high rates of photochemical oxidation (Rissler et al., 2004).

Prenni et al. (2007) have investigated the CCN activity of fresh SOA produced in a smog chamber from toluene and terpene precursors. They found them to be moderately hygroscopic, with κ values around 0.1. From model calculations with mixtures of SOA and sulfate, they conclude that the contribution of SOA to the CCN ability of such mixed aerosols is in most cases indistinguishable from that of insoluble organics. Once incorporated into the condensed phase, the organic compounds are subject to ongoing chemical modification by photochemical and multiphase reactions (Maria et al., 2004; Rudich et al., 2007). This includes oxidation reactions with OH and other radicals (Molina et al., 2004; Zuberi et al., 2005), oligomerization with and without acid catalysis (Claevs et al., 2004b; Gao et al., 2004; Kalberer et al., 2004; Liggio et al., 2007; Surratt et al., 2006), and formation of humic-like substances (HULIS) by photochemical polymerization of biogenic precursors (Gelencsér et al., 2002; Limbeck et al., 2003). These reactions generally tend to reduce the volatility of the organic compounds involved, and render them more polar, thus improving their water solubility and ability to act as CCN (Pang et al., 2006; Sun and Ariya, 2006; Rudich et al., 2007; Duplissy et al., 2008). In some experiments with SOA from terpene oxidation, on the other hand, a decrease of hygroscopicity with photochemical aging has been observed, which may be related to the formation of longer-chained oligomers (VanReken et al., 2005; Varutbangkul et al., 2006). The results from a field study in Canada support that at least some SOA from biogenic precursors can act as CCN at common atmospheric supersaturations (Leaitch et al., 1999).

Recently, a conceptual model has been proposed that involves dynamic and bidirectional exchange of semivolatile organic compounds between the gas and condensed phases, allowing for oxidation reactions in both phases (Donahue et al., 2006; Robinson et al., 2007). Such a mechanism could substantially enhance both the rate and amount of SOA formation.

Despite a large number of experimental and modeling studies on SOA production from biogenic and anthropogenic precursors (Liousse et al., 1996; Griffin et al., 1999b; Kanakidou et al., 2000; Chung and Seinfeld, 2002; Kanakidou et al., 2005; Tsigaridis et al., 2005; Henze and Seinfeld, 2006), the range of estimates of their global source strength remains vast: $2.5-79 \text{ Tg yr}^{-1}$ for biogenic SOA and $0.05-3.5 \text{ Tg yr}^{-1}$ for SOA from anthropogenic precursors. Recent studies suggest

that VOC oxidation in environments with low $[NO]/[HO_2]$ ratios may have substantially larger SOA yields, but still end up with overall SOA production rates within the range given above (Henze et al., 2007). Currently, a conservative best guess might be the values from the review of Kanakidou et al. (2005): 19, 15, and 2 Tg yr⁻¹ from terpenes, oxygenated VOC (OVOC) and anthropogenic VOC, respectively. Given the complexities of particle formation from SOA, and the dependence of SOA formation on the presence of pre-existing aerosol, their contribution to the atmospheric CCN budget can only be estimated using a complete atmospheric model. This will be presented below (Section 2.3.9).

The "consensus view" of SOA production by relatively rapid oxidation processes from predominantly biogenic precursors, as reflected in the review of Kanakidou et al. (2005), has been challenged recently based on observations of surprisingly high organic aerosol concentrations in the free troposphere (de Gouw et al., 2005; Heald et al., 2005). The observed concentrations of about 4 μ g m⁻³ (STP) may require an additional SOA source of ca. 100 Tg C a⁻¹ resulting from slow, continued oxidation or longer-lived VOC (Heald et al., 2005). These results have been complemented by observations of unexpectedly rapid and large production of SOA in an urban environment, presumably from the oxidation of anthropogenic VOC (Volkamer et al., 2006). An even more massive SOA source strength (140–910 Tg C a^{-1}) has been suggested based on mass balance arguments by Goldstein and Galbally (2007). Since neither the precursors nor the reaction mechanisms have been identified to date, these hypotheses still require investigation. Robinson et al. (2007) have proposed that oxidation of semivolatile organics and exchange processes between gaseous and condensed species during photochemical processing may play an important role. The possibility of larger than expected SOA sources is of considerable relevance to our topic, since it would provide a pervasive source of potential CCN both in polluted and remote parts of the atmosphere.

2.3.5. Aerosols from biomass burning

Biomass burning, which comprises open vegetation fires (savannas, forests, and agricultural waste) and domestic biofuel use, is one of the largest sources of aerosol particles worldwide. Pyrogenic (biomass burning) aerosols consist predominantly of carbonaceous material (organic carbon and nearly-elemental "soot" carbon) with a minor component of various inorganic materials (Andreae et al., 1996; Cachier et al., 1996; Mayol-Bracero et al., 2002b; Reid et al., 2005; Sinha et al., 2003; Decesari et al., 2006; Fuzzi et al., 2007). The inorganic component is made up of some insoluble dust and ash material, and soluble salts, in which potassium, ammonium, sulfate and nitrate are the most important species. Of the organic fraction, about half is soluble in water, with a substantial component attributable to dehydrated sugars - essentially cellulose breakdown products such as levoglucosan (Ruellan et al., 1999; Graham et al., 2002; Mayol-Bracero et al., 2002b; Gao et al., 2003; Decesari et al., 2006). While individual particles made up exclusively of inorganic materials or soot are seen in microscopic studies of pyrogenic aerosols, the majority of particles is present in the form of a variety of internal mixtures (Martins et al., 1998; Ruellan et al., 1999; Li et al., 2003).

As a result of their chemical makeup and the prevailing internal mixing, most pyrogenic particles consist of a large fraction of soluble (organic and inorganic) material. Therefore, they are already able to act as CCN immediately over the fires, and become even more easily activated as they age and thereby increase in size and soluble content (Warner and Twomey, 1967; Hobbs and Radke, 1969; Eagan et al., 1974; Hallett et al., 1989; Radke et al., 1991; Rogers et al., 1991b; Ross et al., 2003; Andreae et al., 2004). The fraction of pyrogenic particles that can be activated at S=1% is very high, with most studies showing $CCN_{1\%}/CN$ ratios of 60–100% for fresh or aged biomass smoke (Radke et al., 1988; Rogers et al., 2003; Andreae et al., 2004). This behavior is consistent with their number size spectra, which typically peak in the accumulation

mode size range with number median diameters of 0.1 to 0.2 μ m (Guyon et al., 2005; Reid et al., 2005; Andreae et al., 2007a), and with the fact that their chemical composition is dominated by soluble materials (Rissler et al., 2004, 2006). The hygroscopicity of fresh biomass-burning aerosols covers a wide range, with κ values from ca. 0.01 for some very fresh soot-rich smoke particles to 0.55 for aerosols from grass burning. Currently available results suggest that after some short aging, most pyrogenic aerosols will have κ values in the range of 0.1 to 0.3 (M.O. Andreae, unpublished data, 2007; S. Kreidenweis, unpublished data, 2007). Smoke aerosols also tend to show a distinct coarse mass mode centered around 4 μ m diameter (e.g., Radke et al., 1991), which is, however, unlikely to play a significant role in cloud microphysics.

The source strength for pyrogenic aerosols has been estimated by a number of authors, usually in the context of estimations of the emission of carbonaceous aerosols (Bond et al., 2004; Ito and Penner, 2005; Dentener et al., 2006; Junker and Liousse, 2006; Andreae et al., 2007a). Most studies have used a bottom-up approach, which combines estimates of burned area, fuel loads, burning efficiency, and emission factors to obtain an estimate of the mass of pyrogenic aerosols emitted for specific regions and fire types. Because of the combined uncertainties in these parameters, the overall source strength for pyrogenic aerosols remains quite uncertain, about 30–90 Tg PM2.5 a⁻¹ (Andreae et al., 2007a).

Estimation of the source strength of pyrogenic CCN numbers is in principle relatively straightforward, but also entails large uncertainties. The emission of primary pyrogenic CCN can be scaled using the estimated emission of CO from biomass burning, as the emission ratio of CN to CO is a relatively robust parameter, with a characteristic value of about 25 ± 10 cm⁻³ ppb⁻¹ (Guyon et al., 2005), corresponding to about $2\cdot10^{13}$ particles emitted per gram CO. If we assume an annual global emission of 700 Tg CO from biomass burning (Andreae and Merlet, 2001) and a CCN_{1%}/CN ratio of 0.8, we obtain an estimate of $1.1\cdot10^{28}$ CCN_{1%} for the annual emission from biomass burning. An alternative calculation, based on a CCN_{1%} emission factor of $2\cdot10^{15}$ per kg dry biomass, yields similar results.

In the future, pyrogenic aerosol emissions may rise in some regions, as a warming and possibly drying climate may make vegetation more fire-prone, especially in the temperate and boreal zones. On the other hand, growing environmental concern, an advanced state of tropical deforestation, and a diminishing demand for new agricultural land may result in a slow decline of global emissions from open burning over the 21st century, to about two-thirds of their present values by 2050 (Streets et al., 2004).

2.3.6. Aerosols from fossil fuel combustion

Fossil fuels are burned in industry, power plants, vehicles, and residential heating; about 90% of this takes place in the Northern hemisphere (Andres et al., 1996). Fossil fuel burning in stationary and mobile sources yields a mixture of aerosols, depending on the fuel burned and the combustion technology used (IEA, 1998a,b; Lighty et al., 2000). Coal combustion produces a large amount of ash particles that are mostly in the coarse size range, and which are to a large extent removed by stack technology, especially in developed countries. The dominant submicron primary aerosol emissions, especially from the combustion of petroleum products, are carbonaceous aerosols consisting of soot and organic material (Watson et al., 1994; Cooke et al., 1999; Bond et al., 2004; Junker and Liousse, 2006). Emission estimates vary over a considerable range, from around 6 Tg a⁻¹ (Bond et al., 2004; Ito and Penner, 2005; Dentener et al., 2006) to about 10 Tg a^{-1} (Junker and Liousse, 2006), containing comparable amounts of soot and organic matter. In addition, there are gaseous emissions (SO_2 , NO_x , and hydrocarbons) that contribute to secondary aerosol formation and will be discussed in other sections. Carbonaceous aerosols from fossil fuel combustion, like those from biomass burning, are likely to decline during the 21st century at the global scale, whereas regional increases are predicted particularly in Asia (Streets et al., 2004).

With regard to the production of CCN, the most important primary emissions are the carbonaceous particles, which represent the dominant number emission flux. They consist of a mixture of waterinsoluble, hydrophobic substances (e.g., soot carbon, engine oil, uncombusted petroleum compounds, etc.) (Hudson et al., 1991; Weingartner et al., 1997; Johnson et al., 2005b; Zuberi et al., 2005) and soluble organic and inorganic constituents, particularly H₂SO₄ from the oxidation of the sulfur in the fuels. Depending on the size and composition of these particles, they can have very different CCN properties, leading to considerable disagreement in the literature regarding the hydrophobicity of "fresh soot". Some studies have shown that fresh diesel soot particles are very efficient CCN (Hudson, 1991; Lammel and Novakov, 1995; Hudson et al., 2000), while others find that fresh soot is hydrophobic (Hudson et al., 1991; Weingartner et al., 1997; Zuberi et al., 2005). These differences are in part attributable to different origins of the soots investigated. It appears that very pure hydrocarbon soot, made e.g., by the combustion of CH₄ or hexane (Zuberi et al., 2005; Mikhailov et al., 2006) or jet fuel (Hudson et al., 1991), is initially very hydrophobic. On the other hand, soot particles emitted from diesel engines, and probably most other combustion sources, already contain a modest amount (~3-15%) of soluble organic or inorganic matter (Rogers et al., 1991a; Watson et al., 1994; Lowenthal et al., 1994; Kittelson, 1998; Dua et al., 1999; Sakurai et al., 2003; Petzold et al., 2005). This soluble fraction increases at higher levels of impurities (e.g., sulfur) in the fuels (Schneider et al., 2005). The presence of a significant fraction of sulfate was also used to explain the high CCN activity of the particles in the Kuwait oil smoke plume (Rogers et al., 1991a; Hudson and Clarke, 1992).

The interactions between the primary soot particles and the gaseous pollutants emitted from a diesel engine are illustrated in Fig. 6. Condensation of primary and secondary low-volatile organic species, as well as H₂SO₄ from the oxidation of SO₂, produces internally mixed particles, all of which contain some soluble material.

The small size of some fresh fossil fuel aerosols can also contribute to an initially low CCN efficiency. For example, diesel and gasoline engines typically emit particles with number modal diameters in the ranges of 60–120 nm and 40–80 nm, respectively (Weingartner et al., 1997; Harris and Maricq, 2001; Giechaskiel et al., 2005). In addition, there often is a large nucleation mode in the size fraction <50 nm. This mode may in many cases be an artefact of the exhaust dilution/cooling and sampling process (Kittelson, 1998; Burtscher, 2005), but has also been shown to be a real component of diesel exhaust under highspeed driving conditions (Giechaskiel et al., 2005). These particles consist of sulfuric acid (Giechaskiel et al., 2005), and while they are too small to directly contribute to CCN production, they can add soluble material to other particles, e.g., soot, or become large enough to act as CCN after only very few coagulation steps.

Laboratory studies have shown that it requires only very small amounts, on the order of a monolayer, of soluble substance on the surface of soot particles to substantially enhance their hydrophilicity (Petzold et al., 2005; Mikhailov et al., 2006). Lammel and Novakov (1995) showed that it only takes some 10% of soluble matter to yield a soot particle that has similar CCN activity as an ammonium sulfate particle of comparable size. These authors also suggest that, if a homogeneous mixture of soluble material in their experimental soots are not enough to explain their CCN activity. They propose that other effects, such as the presence of the soluble material as a surface coating and the existence of microcapillary spaces, also contribute to making these particles CCN-active.

The CCN efficiency of the particles increases further during aging, through condensational uptake of soluble substances, coagulation with soluble particles (e.g., sulfates), and chemical reactions (with OH, O_3 , etc.) at the surface (Rogers et al., 1991a; Johnson et al., 2005b; Schneider et al., 2005; Zuberi et al., 2005; Sun and Ariya, 2006; Rudich et al., 2007). Oxidation processes increase both the mass of the

aerosols and the solubility of the organic component (Pang et al., 2006). The timescale of these reactions is still subject to some debate. Older modeling studies tended to assume that the conversion of hydrophobic soot to hydrophilic particles had exponential lifetimes of some 35–80 h (Cooke and Wilson, 1996; Lohmann et al., 2000; Wilson et al., 2001), but recent studies (Riemer et al., 2004; Johnson et al., 2005b) suggest that conversion can occur as fast as 2 h (at daytime in polluted regions), and will rarely require more than 24 h. The uptake of soluble surface coatings on soot particles is greatly enhanced (by about a factor of 4) by the fractal structure of the soot aggregates, as compared to the uptake by spherical particles (van Poppel et al., 2005). This also suggests conversion lifetimes well below 24 h.

Field measurements support the short conversion times predicted by the more recent modeling studies. The droplet-nucleating activity of ambient urban, i.e., slightly aged, soot particles was demonstrated directly using environmental scanning electron microscopy (Ebert et al., 2002). Measurements of scavenging efficiencies in mountaintop clouds in France (Sellegri et al., 2003) showed that in airmasses that had spent 1-2 days over land, 33-74% of EC was scavenged into cloud droplets, compared to 14% of OC and 76-93% of inorganic ions. Moteki et al. (2007) studied the increase in coated soot particles in the plume advecting from the Nagoya, Japan, urban area over the Pacific Ocean and concluded that the particles became internally mixed on a time scale of 12 h. These results suggest that the conventional treatment of soot or BC aerosols in global models, with an initial hydrophobic character that slowly transforms to hygroscopic behavior over time scales of days, is probably obsolete. Given that this transformation occurs at time and space scales smaller than a grid cell in a typical global model, it would be more appropriate to treat carbonaceous aerosols, including soot, as hygroscopic already at the time of emission.

The large emission flux of potential CCN from diesel engines is of concern, especially considering the widespread use of light and heavy duty diesel vehicles in Europe, and the potential for a growing fraction of diesel vehicles in other countries as a result of fuel economy considerations. Depending on the emission control technology used, diesel vehicles can emit several orders of magnitude more particles per distance driven than gasoline vehicles (Harris and Maricq, 2001). With present-day engine designs, the emission of accumulation mode particles is about one order of magnitude larger (on a per km basis) for diesel than for gasoline vehicles (Hudson, 1991; Johnson et al., 2005a; Gertler, 2005). Since diesel particles tend to be larger and contain more sulfur than gasoline engine particles (Zielinska et al., 2004), diesels may contribute an even larger share to CCN. Note that the CCN ability of gasoline engine particles has decreased dramatically after

the elimination of lead additives. Gasoline engine vehicles using leaded gas produce highly soluble particles consisting mostly of lead bromide and chloride, whereas modern gasoline engines emit particles dominated by hydrophobic organics low in sulfur and other water soluble constituents. In a similar way, the widespread use of very-low-sulfur diesel fuel would also significantly reduce CCN production from diesel vehicles.

2.3.7. Sulfates

Most of the atmospheric sulfate aerosol is formed by oxidation of volatile precursors to gaseous H_2SO_4 , followed by nucleation and condensation processes to form particles. In addition, there are minor primary sources of sulfate particles, including the sulfate component of sea salt aerosol, and gypsum or other minerals in dust. These minor sources are, however, only insignificant contributors to the CCN population or have been included in the discussion of the other aerosol types.

2.3.7.1. Precursor gas emissions. Among a variety of gaseous sulfate precursors, only two make a major contribution: dimethyl sulfide (DMS), which is of biogenic origin, and SO₂, for which anthropogenic sources dominate, plus a modest volcanic source (Andreae and Raemdonck, 1983; Bates et al., 1992; Andreae and Crutzen, 1997; Penner et al., 2001; Dentener et al., 2006). Estimates of the biogenic emission of DMS typically fall in the range 20–35 Tg S a^{-1} (Andreae, 1990; Bates et al., 1992; Kettle and Andreae, 2000; Simó and Dachs, 2002; Boucher et al., 2003; Belviso et al., 2004). The discovery of a potential feedback loop between biogenic DMS production, the abundance of sulfate CCN over the oceans, cloud physics, and climate has been a major stimulus for research into the interactions between aerosols and climate (Charlson et al., 1987). Because of the complexity of the interactions between marine plankton ecology and DMS production, however, the magnitude and sign of this feedback remains still an unsolved puzzle. A recent modeling study has suggested that the climate warming resulting from a tripling of atmospheric CO₂ by the end of this century would result in an increase of DMS flux by 14% (Gabric et al., 2004), but this must be seen mostly as a sensitivity study. At the present state of knowledge, we can only state that, because sulfate aerosols from the oxidation of DMS make up a major fraction of CCN particles in remote marine regions (Andreae et al., 1995, 1999, 2003; Prospero et al., 1991; Avers et al., 1997; Jourdain and Legrand, 2001; Vallina et al., 2006), they must play an important role in regulating cloud properties and precipitation over the pristine oceans. The response of these linkages to past and future climate change, however, remains unclear.



Fig. 6. Interactions between the soot particles emitted from a diesel engine and the co-emitted sulfur gases and organic species (from Schneider et al., 2005).

Volcanic sulfur emissions, predominantly in the form of SO₂, are considered to be in the range of 8–20 Tg S a⁻¹ (for a review, see Textor et al., 2004). Because much of this SO₂ is emitted from mountain tops in the free troposphere, it is less subject to dry deposition and is therefore more efficiently converted to sulfate than most anthropogenic SO₂ (Penner et al., 2001).

Over the past century, SO₂ emissions from anthropogenic sources have grown dramatically, from less than 10 Tg S a^{-1} in 1890 to about 70–75 Tg S a^{-1} in 2000 (Grübler, 1998, 2002; Smith et al., 2001; Benkovitz et al., 2004; Dentener et al., 2006; Ganzeveld et al., 2006). Emissions are dominated by the burning of fossil fuels, particularly coal (53 Tg S a^{-1}), with minor additional sources from smelting, biomass burning, and paper production. The SO₂ emissions from ship traffic are also a relatively minor source in terms of their total amount (ca. 4 Tg S a^{-1}), but because of the fact that they are released into otherwise fairly unpolluted marine regions, they make a substantial contribution to the aerosol budget in remote areas (Capaldo et al., 1999; Endresen et al., 2005).

Globally, SO_2 emissions have remained nearly constant over the last three decades, and may even have begun to decline. This is the result of two sharp, opposing trends: a rapid decrease as a result of emission controls and economic change in the OECD countries and the Eastern European and FSU states (e.g., Vestreng et al., 2007), and a dramatic increase in the developing world, especially China and India (Streets et al., 2000; Streets and Waldhoff, 2000; Massie et al., 2004; Stern, 2006). In spite of rapid economic growth in China, there are signs that the increase in SO₂ emissions is slowing (Carmichael et al., 2002; Streets and Waldhoff, 2000; Stern, 2006). Chinese government policies are calling for stringent emission controls by 2010, but whether these goals can be accomplished remains unclear. A global reduction in the emission of aerosol precursors, especially SO₂, is also suggested by recent observations of increasing transparency of the atmosphere (Wild et al., 2005; Mishchenko et al., 2007).

2.3.7.2. Formation of sulfate particles. While there is fairly good agreement in the literature with regard to the magnitude of sulfate precursor emissions, the estimates of production rates and burdens of sulfate aerosols show considerable variation (Barrie et al., 2001; Penner et al., 2001; Berglen et al., 2004; Kinne et al., 2006). The most recent model intercomparison exercise, AeroCom, yielded a range of 50–81% for the fraction of SO₂ transformed into sulfate, with the differences being mostly due to variations in the treatment of SO₂ dry deposition between models (Kinne et al., 2006; Textor et al., 2006). These models predict a sulfate source of 180 Tg SO₄ a⁻¹ (±22%), and a global sulfate burden of 1–3 Tg SO₄. Other models, which did not participate in AeroCom, yield similar results, e.g., Rotstayn and Lohmann (2002).

Besides the fraction of SO₂ converted to sulfate, the specific mode of transformation also has a major influence on the climatic impact of the sulfate aerosol produced. There are two relevant pathways, the oxidation of SO₂ in the gas phase by OH to gaseous H₂SO₄, and the oxidation in the liquid phase in cloud droplets or deliquesced aerosols by O₃ or H₂O₂. Formation of new particles by nucleation can only occur via the first pathway, gas-phase oxidation, and then only if the gaseous H₂SO₄ is not scavenged by pre-existing aerosol surfaces before it has a chance to undergo nucleation to aerosol particles. As a result of these complexities, the same amount of sulfate can have very different climatic effects. On one extreme, if SO₂ conversion happens on pre-existing large particles or in droplets grown on such particles, the cloud physical effect of the added sulfate is practically nil. On the other hand, a very small amount of sulfuric acid can result in the nucleation of a large number of ultrafine H₂SO₄ particles, which can make possible the subsequent deposition of organic semivolatile compounds, essentially catalyzing the formation of SOA particles (see also Section 2.3.4) (Kulmala et al., 2004a; Boy et al., 2006).

It is clear from this discussion, that a meaningful analysis of the production of cloud-active particles from the emission of SO₂ is not

possible based on a simple and isolated analysis of mass fluxes, but has to be conducted within a model that simulates interactions between aerosol species and meteorological processes (Wilson et al., 2001; Stier et al., 2005). An analysis of the difference in aerosol burden between model runs with and without anthropogenic SO₂ (Stier et al., 2006a; Andreae et al., 2007a) suggests that anthropogenic sulfates account for an estimated 25-30% of the accumulation mode particle burden in the region between 0° and 60°N. Globally, omission of anthropogenic SO₂ reduced the accumulation mode number burden by 21% in this model. The results of Wilson et al. (2001) suggest that the production rate of sulfate-containing CCN (accumulation mode particles) is of the order of $2 \cdot 10^{28}$ a⁻¹. Since part of the Aitken mode (down to diameters of about 50 nm) can also contribute to the CCN population, and since even a modest amount of sulfate can dramatically improve the CCN ability of otherwise poorly soluble particles, more detailed modeling studies will be required to determine the contribution of anthropogenic SO₂ to the CCN budget.

2.3.7.3. Biogenic sulfur emissions and the remote marine aerosol. The number size distribution of the remote marine aerosol is characterized by the presence of three major size modes (Heintzenberg et al., 2000, 2004). The smallest, referred to as the "aged-nucleation" or Aitken mode, is centered around 30–50 nm, and has been thought to arise from in-situ particle nucleation associated with gas to particle conversion under conditions of low pre-existing aerosol surface area (Hoppel and Frick, 1990; Wiedensohler and Covert, 1996; Brechtel et al., 1998; Clarke et al., 1998). The accumulation mode, in the size range from about 100–200 nm diameter, is made up to a large extent from DMS-derived non-sea salt sulfate (Andreae et al., 1995, 1999, 2003; Andreae and Crutzen, 1997; Bates et al., 2002). Its modal characteristics are thought to result from cloud processing of the marine aerosol (Hoppel et al., 1986, 1990, 1994; Hoppel and Frick, 1990). Finally, the sea salt number mode is centered at 200–500 nm dry diameter (see Section 2.3.2).

In the original formulation of the CLAW hypothesis (Charlson et al., 1987), it was assumed that the submicron marine aerosol consisted predominantly of sulfate from the oxidation of biogenic DMS, with a minor contribution from the submicron part of the sea salt distribution. These particles were thought to originate by the nucleation of particles from gaseous H₂SO₄, and subsequent growth by coagulation, condensation and cloud processing. The more recent findings of significant amounts of organic matter in the accumulation and especially the Aitken mode, and the presence of sea salt down into the size range <100 nm (Murphy et al., 1998a,b; Cavalli et al., 2004; Leck and Bigg, 2005a; Lohmann and Leck, 2005; Clarke et al., 2006) have called this view into guestion. It now appears likely that nucleation of sulfate particles in the marine boundary layer is relatively rare, and that inputs of small particles (organic and salt) from the sea surface and downward mixing of particles from the free troposphere play a crucial role (Clarke et al., 2006; Pierce and Adams, 2006). The main role of DMS oxidation may be to provide H₂SO₄ for the condensational growth of smaller particles, which ultimately facilitates droplet nucleation at the small supersaturations found in marine stratus.

Recently, an additional source of marine biogenic aerosols has been suggested by Meskhidze and Nenes (2006). Based on remote sensing observations, they suggest that the oxidation of isoprene released by phytoplankton can produce enough secondary organic aerosol to significantly affect marine CCN concentrations and cloud properties. The results of this study have been called into question, however, because an incorrect assumption produced an error of three orders of magnitude in the authors' calculations (Wingenter, 2007).

2.3.8. Minor aerosol species

2.3.8.1. Industrial dust. The category of "industrial dust" includes a broad variety of anthropogenic primary aerosols, particularly those from transportation (e.g., tire and brake detritus, road dust, etc.), coal

combustion (fly ash, etc.), cement manufacturing, metallurgical industries, and waste incineration. Such aerosols are prominent in uncontrolled emissions from old industrial and energy technology, but are now being controlled fairly tightly, especially in developed countries. A very rough estimate of 100 Tg a^{-1} for the emission of this aerosol type was given in IPCC-TAR (Penner et al., 2001). Unfortunately, there are no recently updated global emission estimates, and no data are available on which a reliable estimate of the number source flux for this particle type could be based. The mass size distribution of these aerosols is dominated by the coarse mode, but a substantial submicron mode is also present, which contains significant amounts of soluble material (Kleeman and Cass, 1998; Chen et al., 2004).

Growing industrialization, especially in Asia, has been expected to result in significant increases of industrial dust. In Beijing, for example, primary aerosols have been estimated to account for more than half of PM2.5 (Zhang et al., 2004c). On the other hand, increased awareness in developing countries of the adverse health impacts of aerosols, coupled with readily available emission control technology, may lead to less significant growth in these emissions than had been previously anticipated (Wolf and Hidy, 1997). We conclude that primary anthropogenic particles could represent a significant source of CCN (and possibly IN), especially in polluted regions of the developing world, but that future increases are likely to be constrained by environmental concerns.

2.3.8.2. Nitrate. Nitrate has, until recently, not been considered in assessments of the climatic effects of aerosols. Even current models often ignore the role of nitrate (e.g., Stier et al., 2005; Textor et al., 2006), or assume that it is only present in the coarse fraction (Derwent et al., 2003). Yet, recent model estimates of the atmospheric burden of the CCN-relevant submicron nitrate are not negligible compared to the sulfate burden of ca. 1 Tg SO₄²⁻. Adams et al. (2001), predicts a nitrate burden of 0.38 Tg in the form of secondary ammonium nitrate/sulfate particles and Bauer et al. (2007) estimate a burden of 0.49 Tg, while Metzger et al. (2002a) arrive at a much lower estimate of ca. 0.15 Tg NO₃.

While SO_2 emissions are fairly easy to reduce because they are strongly tied to large point sources (power plants), the emissions of NO_x , the precursor of aerosol nitrate, have proven much more difficult to control. This suggests that the importance of aerosol nitrate is likely to increase substantially over the current century (Bauer et al., 2007). For example, the SRES A2 emissions scenario projects that NO_x emissions will more than triple by 2100, while SO_2 emissions will decline slightly. Using this scenario, Adams et al. (2001) predict a nitrate burden of 1.8 Tg for 2100, compared to a sulfate burden of 2.2 Tg for the same year. In their model run for 2100, the total anthropogenic forcing (direct and indirect) associated with nitrate actually exceeds that caused by sulfate.

Aerosol nitrate can occur either as a component of the coarse particle fraction, where it is present as a reaction product with sea salt or mineral dust, or as ammonium nitrate, NH₄NO₃, in the sub-micron size fraction (Kleeman et al., 1999). Its influence on cloud microphysics is fundamentally different for each case. In sea salt particles, nitrate simply replaces chlorine, and the CCN properties of the chemically modified particles are not significantly different from the original SSA. In contrast, the deposition of nitric acid, HNO₃, on otherwise insoluble dust particles, which is favored in atmospheres rich in dust and low in gaseous ammonia, NH₃, sharply increases their CCN activity (Dentener et al., 1996; Murphy and Thomson, 1997; Gard et al., 1998; Zhang et al., 2003; Laskin et al., 2006).

The production of secondary aerosol nitrate in the sub-micron fraction is strongly dependent on the abundances of gaseous NH_3 and HNO_3 , particulate H_2SO_4 , temperature and humidity (ten Brink et al., 1996; Clegg et al., 1998; Metzger et al., 2002b; Zhang et al., 2002; Bauer et al., 2007). If ammonia is available in excess of the amount required to neutralize the stronger acid H_2SO_4 , gaseous HNO_3 and NH_3 can enter the condensed phase, and their subsequent dissociation

yields nitrate (NO₃) and ammonium (NH₄⁺) ions. Condensation of NH₄NO₃ is expected to occur onto pre-existing particles, rather than by homogeneous nucleation (Kleeman et al., 1999). Submicron particles containing nitrate are efficient CCN, both as separate NH₄NO₃ particles or in internal mixtures (Metzger et al., 2002a). Therefore, while this process does not increase the total particle number, it is likely to increase the fraction of particles that are CCN.

2.3.9. Integrated aerosol source models

In the previous sections, we have seen that the rate of CCN production is not a question that can be addressed in the classical way of assembling databases of emission factors and activity estimates. Rather, the number of CCN produced is regulated by the complex interplay of the emission of primary particles, nucleation of new particles, condensation of secondary gaseous species, and interactions between aerosol particles. Therefore, an analysis of the sources and burdens of cloud-active particles requires the use of a comprehensive atmospheric model that accounts for all these processes. This model must carry, either explicitly or in parameterized form, information about the number/size distribution of soluble and wettable materials, ice-nucleating ability, and the interactions between gas phase and various condensed phases. The most meaningful representation of a source strength for a particular component is then based on the difference between particle fluxes with a given source or precursor (for example anthropogenic SO_2) turned on or off in a full atmospheric model, as has been done by Stier et al. (2006a).

Unfortunately, this type of approach is still in its infancy, and is often only applied to subsets of the atmospheric aerosol spectrum, or without explicit treatment of size-resolved number fluxes and burdens (Ghan et al., 2001; Wilson et al., 2001; Metzger et al., 2002a; Derwent et al., 2003; Textor et al., 2006). Only recently have some fairly comprehensive global aerosol models become available that include explicit representation of the number size distributions of aerosols (Adams and Seinfeld, 2002; Gong et al., 2003; Herzog et al., 2004; Rodriguez and Dabdub, 2004; Spracklen et al., 2005; Lauer and Hendricks, 2006; Verma et al., 2007).

One of the most complete analyses (suitable for long-term climate simulations) to date is represented in the aerosol-climate model ECHAM5-HAM (Stier et al., 2005). In this model, the major aerosol components sulfate, particulate organic matter (POM), black carbon (BC), sea salt, and mineral dust are determined through an aerosol module that is interactively connected to a climate model. A similar approach has been recently published by Lauer and Hendricks (2006), who combined the ECHAM4 general circulation model with the Modal Aerosol Dynamics Module (MADE). These models are able to give a first indication of the global distribution of potentially cloud-active aerosols (Fig. 7), but still face shortcomings due to the highly parameterized modal treatment of size distributions. Given the strong dependence of CCN activity on particle size (Dusek et al., 2006), improved size resolution is highly desirable, but comes at great computational cost. Improvements may also be required in the treatment of nucleation processes, which often have been treated in a highly simplified manner. Spracklen et al. (2005a, 2006) have argued that this leads to a serious underestimation of the importance of nucleation in the remote boundary layer, with still unexplored consequences for the CCN budget of the clean continental atmosphere.

2.4. Anthropogenic vs. natural aerosol populations: what would the atmosphere be like without human pollution?

In order to assess the effect of anthropogenic aerosols on clouds and precipitation, we need to know what the aerosol content of the atmosphere would be like in the absence of human activities. Knowledge of the pre-human and pre-industrial aerosol burden is of particular importance to an assessment of the cloud-mediated aerosol effects on climate, since cloud properties respond to aerosols in a nonlinear way, and are most sensitive to the addition of particles when the background concentration is very low (Twomey and Squires, 1959; Menon et al., 2002; Lohmann and Feichter, 2005).

Unfortunately, information about aerosol loadings in the absence of human activity is very difficult to obtain (Andreae, 2007a). Not long ago, any environment outside of the immediate vicinity of pollution sources was thought of as pristine. It is now very clear that quite the opposite is true: Because of the huge amount of anthropogenic emissions of aerosol particles and their gaseous precursors, combined with efficient long-range transport, it is very difficult to find areas on Earth, especially on the continents, that are not impacted by pollution aerosols. Aerosol particles have typical atmospheric lifetimes of 3-10 days, depending on their size, solubility, location, etc. (Andreae, 1995). This does not mean, however, that after this period of time all particles will have been removed from the atmosphere, but that their number will have decreased to a specified fraction of its initial value (often to 37%, or 1/e, if the lifetime is defined as an e-folding lifetime in an assumed first-order removal process). This implies, however, that even after 3 "lifetimes" about 5% of the initial burden is still left. Given that airmasses can easily travel several 1000 km in 15 days, and that, at least in the northern hemisphere, few places are more than a few 1000 km from major pollution sources, there are really no places where we can expect to find truly pristine conditions in the northern hemisphere. This is supported by model calculations, which show that there is no region without significant anthropogenic sulfate pollution anywhere over the Northern Hemisphere (e.g., Spracklen et al., 2007).

There are two principal methods for investigating the aerosol content of the pristine atmosphere: 1) careful analysis of the number and mass concentrations of aerosols at the sites presumably least impacted by anthropogenic emissions, looking for periods when pollution impacts are minimal, and 2) model predictions from aerosol models of the type discussed in Section 2.3.9, run without anthropogenic emissions. We shall look at both of these approaches in turn.

2.4.1. Aerosol observations in the remote atmosphere

Aerosol concentrations approaching pristine conditions are most easily found over the oceans, especially in the Southern Hemisphere, where large expanses of open ocean and a low density of population and industry both contribute to keeping the human impact at a minimum. As discussed in previous sections, the natural aerosol over the remote oceans consists mainly of a mixture of sea salt particles, primary and secondary organics, and sulfates from the oxidation of DMS and some other natural sulfur emissions. Depending on the region, mineral dust and biomass smoke may also be present, even in the pre-human atmosphere. There are extensive measurements of aerosol number concentrations, size spectra, and CCN concentrations



Fig. 7. Climatological annual means of simulated accumulation mode aerosol particle concentration obtained from a 10-year integration. The geographical distribution of the lowermost model layer (upper panel), which is about 60 m thick, and the zonally averaged vertical cross section (lower panel) are shown. The concentrations are given at STP conditions (from Lauer and Hendricks, 2006).

in remote marine regions (Twomey and Wojciechowski, 1969; Hoppel, 1979; Gras, 1990; Hoppel and Frick, 1990; Hegg et al., 1991; Gras, 1995; Jennings et al., 1998; Hudson and Xie, 1999; Hudson and Yum, 2002; Yum and Hudson, 2004). In biologically more productive seasons and regions, typical CCN concentrations are in the low hundreds cm⁻³ at S = 1% (and correspondingly less at lower *S*), while in winter a few tens of CCN_{1%} per cm³ are typically found (Fig. 2). When pollution aerosols are present, either transported from the continents or from the emission of ships, CCN concentrations in marine regions can reach several thousands cm⁻³ (Hudson and Xie, 1999; Hudson et al., 2000; Hudson and Yum, 2002).

Evaluating pristine CCN concentrations over continental regions is a much more difficult problem. Measurements at sites away from obvious sources of pollution are very few, and even among these data, it is usually difficult to assess how much of the observed aerosol is due to pollution. Aerosol composition at many remote sites in the northern hemisphere suggests that the continental "background" aerosol nowadays consists mostly of pollution aerosols at varying levels of dilution. For example, a study of the European aerosol climatology shows that the average PM2.5 concentration ranges from some 30 µg m^{-3} at urban sites to about 4 µg m^{-3} at the cleanest site, Sevettijärvi in northern Finland (Putaud et al., 2004; Van Dingenen et al., 2004). The composition of the aerosol at this remote site is, however, very similar to that at urban and regionally polluted sites, with a large fraction of non-sea salt sulfate, and about 4% of the combustion tracer black carbon. Even in the Southern Hemisphere, pollution aerosols dominate in most continental areas, especially in the dry seasons, when biomass burning is extremely widespread (Artaxo et al., 1988, 1994, 2002; Sinha et al., 2003). CN and CCN concentrations are typically in the upper hundreds to thousands cm⁻³ under these conditions (Sinha et al., 2003; Andreae et al., 2004).

Only under relatively rare circumstances do aerosol concentrations over the remote continents approach pristine conditions. This usually occurs when clean marine airmasses are advected over practically uninhabited continental regions. Examples are the rainy season in central Amazonia, some of the desert regions in Australia and parts of the boreal regions in Eurasia and North America. Measurements made in the center of the Amazon Basin during the rainy season, when clean airmasses from the Atlantic Ocean are transported for several days over the Amazon forest across virtually uninhabited regions, showed CCN concentrations in the low hundreds, more or less identical to the levels over the tropical ocean (Roberts et al., 2001). Low CCN concentrations have also been reported from other continental sites. At a rural site in SE Australia, Twomey et al. (1978) found CCN_{0.8} concentrations of 200–300 cm⁻³ in the background wind sectors. Upwind of Denver, Colorado, CCN075 concentrations were 300-400 cm⁻³ at 500–2000 m above ground level (Squires and Twomey, 1966). In a later study in the same area, somewhat higher concentrations were found (400-500 cm⁻³) (Frisbie and Hudson, 1993). Balloonborne measurements over Wyoming showed average CCN levels of 445 and 146 for the summer and winter lower troposphere, respectively (Delene and Deshler, 2001). Over the Yukon Valley, Alaska, Hoppel et al. (1973) measured $CCN_{0.7}$ concentrations of around 150 cm⁻³. For the Eurasian continent, few remote measurements exist. The only valid data come from northern Finland, where average CCN concentrations of the order of 90–150 cm⁻³ can be inferred from the studies of Lihavainen et al. (2003) and Komppula et al. (2005).

Clearly, all these measurements represent upper limits to the "natural" CCN populations, as all these locations must be considered anthropogenically influenced to various degrees. Even where local influences can be excluded, long-range transport, even on an intercontinental scale, is affecting background concentrations at remote sites. Measurements have shown that sulfate aerosols from Asia can dominate the tropospheric sulfate burden at the West Coast of North America (Andreae et al., 1988; Jaffe et al., 2003), and model simulations suggest that Asian pollution contributes more than 30% of

the surface sulfate over an extended area in the North Pacific and North Indian Oceans and between 10 and 30% over the Arctic (Chin et al., 2007).

An alternative way of assessing the natural continental CCN background is through estimation of the number of new particles in the CCN size range produced from biogenic precursors at a remote site. This approach has been used by Kerminen et al. (2005) at the Pallas site in northern Finland. They concluded that newly formed particles grew to a size large enough to act as CCN during 15-25% of the ca. 40 new particle formation events occurring annually at this site. On average, 180 ± 150 cm⁻³ particles were produced during these events, clearly not enough to sustain a significant CCN population on a continuous basis. In a more representative analysis, Tunved et al. (2006) determined the increase in the number of particles as airmasses traveled over land from the Atlantic coast to receptor sites in Finland. They found that particle number increased with travel time and with the rate of terpene emission. At typical emission rates, concentrations of about 1000-2000 cm⁻³ were reached, of which about 100-300 were larger than 90 nm and therefore probably CCN at intermediate supersaturations. Given that these data are from a region where nucleation is favored because of trace amounts of anthropogenic SO₂, and that they only apply to the spring and summer seasons, these values probably still represent an upper limit to natural CCN production at mid-latitudes. Overall, we conclude that natural production of CCN-active particles over biologically active regions on the continents can probably not account for more than 100–300 cm⁻³ in most cases, not much greater than the levels found over the oceans. During the cold seasons, much lower particle production must be expected.

2.4.2. Model estimates of pre-human aerosol abundance

Global aerosol models have initially focused on anthropogenic aerosols, especially sulfate, and have only in recent years begun to incorporate natural sources. Among natural aerosol components, sea salt, soil dust, biomass smoke and sulfate from DMS have been investigated fairly extensively, while secondary organic aerosols and primary biogenic aerosols are still very poorly understood. Since these two components may be responsible for a large fraction of the natural continental aerosol, the current model estimates of continental aerosol abundance are probably not very reliable. This applies especially to aerosol number concentrations and size distributions, which are our primary concern here.

There are no studies that have attempted to look at the atmosphere before the advent of humans. We therefore have to either consider as our reference state the pre-industrial period (e.g., Stier et al., 2006b; Tsigaridis et al., 2006) or the present-day atmosphere with anthropogenic sources turned off in the models (Wilson et al., 2001; Park et al., 2006; Chin et al., 2004). Some useful information can also be obtained by looking at the regions least influenced by anthropogenic emissions (e.g., northern Eurasia and North America) in model studies that do not provide results on non-anthropogenic conditions (e.g., Lauer and Hendricks, 2006). All models agree that anthropogenic emissions have caused large enhancements of aerosol loads even over the remote continents, with typical enhancements of 50-300% over remote regions of Asia, North America, and South America (Wilson et al., 2001; Chin et al., 2004; Park et al., 2006; Stier et al., 2006b). In addition to enhanced aerosol burdens, model calculations also suggest that present-day aerosols contain 2.7 times more inorganic components than in preindustrial times, making them more efficient CCN (Tsigaridis et al., 2006).

From these studies, we can estimate pre-industrial concentrations of $50-200 \text{ cm}^{-3}$ for particles in the CCN size range over the continents (Wilson et al., 2001; Lauer and Hendricks, 2006), which is not significantly different from the values over the remote oceans in the same models. Such low number concentrations are consistent with the low natural mass concentrations predicted by those models that

do not explicitly provide particle number concentrations – they predict values typically less than 1 μ g m⁻³, and suggest also relatively little difference between oceans and continents at the same latitude (Park et al., 2006; Stier et al., 2006b). Higher aerosol concentrations are predicted over the tropical continents because of already elevated levels of biomass burning in pre-industrial times. It is difficult to estimate what the smoke emissions from natural vegetation fires would have been before the advent of humans and the deliberate use of fire by early hominids, but it is likely to be considerably lower than even the pre-industrial values.

3. Summary and conclusions

The subset of particles from the overall aerosol population that can act as CCN is determined mostly on the basis of the number of soluble molecules a particle contains, which in turn is a function of particle size and chemical composition. The complexity and variability of the composition of ambient aerosols makes an explicit treatment of chemical properties in CCN models practically impossible. Recent studies have shown, however, that for the purpose of assessing CCN activity, the effects of aerosol composition can be represented by a single parameter, e.g., the hygroscopicity parameter, κ (Petters and Kreidenweis, 2007). This makes it possible to estimate CCN spectra based on knowledge of this parameter and the ambient size distribution.

Studies with instruments that determine the CCN concentration as a function of both supersaturation and particle size suggest that continental and marine aerosols tend to cluster into relatively narrow ranges of hygroscopicity (Section 2.1.3), which facilitates their treatment in atmospheric models. It must be emphasized, however, that knowledge of the chemical composition of aerosols is essential in order to determine aerosol sources and production mechanisms and to assess the role of anthropogenic versus natural contributions to the atmospheric aerosol burden.

The pervasive presence of anthropogenic aerosols, especially in the Northern Hemisphere, makes it very difficult to obtain qualitative and quantitative observations of the characteristics and concentration of the natural aerosol population (Andreae, 2007b). However, both model predictions and observations suggest that natural aerosol and CCN concentrations are quite low, and don't differ strongly between land and ocean regions. This is evident even nowadays in the global aerosol distribution observed by spaceborne sensors such as MODIS and MISR (Fig. 8). Here we see the global annual-average distribution of aerosol burdens represented as aerosol optical thickness, i.e., the extinction of sunlight by atmospheric aerosols (Kinne et al., 2006). It is remarkable that continental areas per se do not stand out in this image, as one would have expected from the conventional view of continents being characterized by high aerosol burdens. For example, western North America, southern South America and southern Africa, and most of Australia have more or less the same aerosol burdens as the surrounding oceans. High aerosol loads over the continents are found in and downwind of regions with specific sources, such as the dusty regions in subtropical Africa and Asia, the biomass burning regions in the tropical continents, and the industrialized regions concentrated at northern mid-latitudes.

Natural aerosol concentrations over the oceans, away from dust and smoke sources, are probably similar to those found now only over the Southern Hemisphere Oceans: 50–200 CCN cm⁻³, consisting mostly of a mixture of sulfates from DMS, organics and salt particles. Over the continents, we expect natural aerosol concentrations of some 100–300 CCN cm⁻³, mostly from biogenic sources (primary biological particles, secondary particles from the oxidation of DMS, H₂S, and VOC) (Andreae, 2007a). At some times and places, of course, desert dust and smoke from wildfires would dominate the natural aerosol populations. The lowest CCN concentrations in the unpolluted atmosphere occur when and where biological activity is at a minimum, e.g., in wintertime or over desert areas, where typical CCN concentrations are only a few tens per cm³. Extremely low CCN levels are also found in those regions where feedback processes lead to very high scavenging efficiency (Rosenfeld et al., 2006). Clearly, even quite small emission sources, such as wood burning in winter or ship emissions over the remote oceans, can lead to a dramatic increase in aerosol concentrations at such low background levels.

The low natural CCN concentrations over the continents render invalid the conventional classification into "maritime" and "continental" air masses by their aerosol content. It also implies that the high aerosol concentrations typically found nowadays over most continental areas are largely anthropogenic. Consequently, before the



Fig. 8. Global distribution of atmospheric aerosols represented as aerosol optical thickness, i.e., the extinction of sunlight by atmospheric aerosols. The image was obtained by merging data from several satellite sensors with ground-based sunphotometer measurements (figure courtesy of S. Kinne pers. comm., 2006).

onset of anthropogenic pollution, cloud microphysical properties over the continents probably resembled those over the oceans, whereas cloud processes over most of the present-day continents mostly reflect the effects of human perturbation.

In the companion paper (Rosenfeld and Khain, in preparation), we will explore the consequences of this perturbation for precipitation processes and climate. We will also discuss a number of feedbacks, by which the concentration of CCN affects the removal flux of aerosol particles from the atmosphere, and thus the CCN burden itself. We have already mentioned in Section 2.1.4 the role that sea salt giant CCN can play in facilitating the scavenging of pollution aerosols in the marine boundary layer. Another example is the bi-stable behavior of boundary layer aerosol concentrations. At low CCN concentrations, nucleation scavenging of aerosols and removal by rain drop production are very effective, whereas elevated aerosol concentrations result in high fractions of interstitial aerosol and inefficient aerosol removal by rainfall over both land and oceans (Andreae et al., 2004; Rosenfeld et al., 2006). This results in a bi-static stability behavior where very low aerosol concentrations are maintained as long as aerosol inputs are low, with a sharp transition into a high aerosol regime occurring when aerosol inputs exceed a threshold level. Another feedback process may occur when elevated CCN concentrations, especially from biomass smoke, enhance the likelihood of lightning strikes, which then can ignite vegetation and lead to further smoke production (Lyons et al., 1998; Vonnegut et al., 1995; Murray et al., 2000; Williams and Stanfill, 2002; Smith et al., 2003; Williams and Sátori, 2004; Rosenfeld et al., 2007b).

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