The relative importance of non-sea-salt sulphate and sea-salt aerosol to the marine cloud condensation nuclei population: An improved multi-component aerosol–cloud droplet parametrization

By COLIN D. O’DOWD1*, JASON A. LOWE1, MICHAEL H. SMITH1 and ANDREW D. KAYE2

1University of Sunderland, UK
2DRA Farnborough, UK

(Received 29 August 1997; revised 6 July 1998)

SUMMARY

The effect of sub-cloud aerosol on cloud droplet concentration was explored over the north Atlantic and east Pacific under a variety of low and high wind speed conditions. A relationship of the form of $D = 197(1 - \exp(-6.13 \times 10^{-3} * A))$ was found to fit best the relationship between cloud droplet concentration ($D; \text{cm}^{-3}$) and sub-cloud aerosol concentration ($A; \text{cm}^{-3}$) under low to moderate wind conditions. A few noticeable deviations from this relationship were observed which occurred under moderate to high wind speed condition. Under these high wind conditions, sea-salt aerosol provided the primary source of cloud nuclei due to their higher nucleation activity and larger sizes, even under sulphate-rich conditions. Simple model simulations reveal that the activation of sea-salt nuclei suppresses the peak supersaturation reached in cloud, and thus inhibits the activation of smaller sulphate nuclei into cloud droplets. A multi-component aerosol–droplet parametrization for use in general circulation models is developed to allow prediction of cloud droplet concentration as a function of sea-salt and non-sea-salt (nss) sulphate nuclei. The effects of enhancing an existing nss-sulphate cloud condensation nuclei (CCN) population with sea-salt nuclei are to reduce the number of cloud droplets activated under high (polluted) sulphate conditions and to increase the cloud droplet concentration under low (clean) sulphate conditions. The presence of sea-salt CCN reduces the influence of nss-sulphate CCN on cloud droplet concentrations, and thus is likely to reduce the predicted effect of nss-sulphate indirect radiative forcing.

KEYWORDS: Aircraft observations  Cloud processes

1. INTRODUCTION

Marine low-level stratiform clouds contribute significantly to the planetary albedo (Slingo 1990), and consequently perturbations in their reflectance can potentially modify the earth’s radiative budget. Cloud optical properties are controlled by the mean effective radius of the cloud droplet distribution which, in turn, is controlled by the availability of cloud condensation nuclei (CCN) for a given liquid water content (Twomey 1974). It is generally assumed that non-sea-salt (nss) sulphate, both natural and anthropogenic, dominates the marine CCN population. Natural nss-sulphate is derived from the oxidation of sulphur dioxide ($\text{SO}_2$), an oxidation product of dimethyl sulphide (DMS) which is produced as a product of the marine biota metabolism. Anthropogenic sulphate in the marine environment results from long-range transport of $\text{SO}_2$ and sulphate aerosols.

Twomey et al. (1984) suggested that an increase in pollution emissions, and thus an increase in available sulphate CCN, would lead to a reduction in the effective radius of cloud droplets, and thus to brighter clouds, thereby resulting in a planetary cooling. This cooling effect is thought to be of similar magnitude to the radiative forcing induced by greenhouse gases, but opposite in sign. Charlson et al. (1987) also postulated that a natural negative feedback mechanism may exist where global warming, resulting from increased $\text{CO}_2$ emissions, could be offset by an increase in biogenic nss-sulphate CCN over the oceans which may ensue from increased biological activity in warmer oceanic waters, and consequently an increase in the emission rate of DMS.

Because of the potential effect of increased $\text{SO}_2$ and sulphate aerosol emissions, it is desirable to know accurately, and be able to predict, the radiative forcing induced by increased anthropogenic activity. Recent attempts to predict anthropogenic sulphate

* Corresponding author: Centre for Marine and Atmospheric Sciences, School of the Environment, University of Sunderland, Sunderland, Tyne and Wear SR2 7BW, UK.
radiative forcing have resulted in an estimated cooling of between $-0.5$ and $-1.5 \text{ W m}^{-2}$ (Jones et al. 1994; Boucher and Lohmann 1995). One possible source of error in these studies is, however, in assuming that nss-sulphate aerosol, particularly over the ocean, is the primary source of CCN. This assumption may lead to an overestimation of the radiative forcing by sulphate aerosol if there is a significant contribution to the CCN population from other sources.

Early studies on the production of sea-salt nuclei were conducted by Woodcock (1953), Blanchard and Woodcock (1957), Blanchard (1963), and Blanchard and Woodcock (1980). In their findings, they concluded that wind stress at the ocean surface produces entrained air bubbles that, on bursting after rising to the surface, generate film drops and ‘jet’ sea-salt drops. These salt drops are generated at the onset of ‘whitecapping’ at wind speeds of about $3 \text{ m s}^{-1}$. These, and later investigations, found the production of sea-salt nuclei to be related exponentially to wind speed over the ocean (Woodcock 1953; Gras and Ayers 1983; Exton et al. 1985; and Smith et al. 1989). Blanchard and Woodcock (1980) presented vertical distributions of sea-salt mass for different wind speed conditions. They found that the slope of this vertical distribution varied between zero and negative gradient values, however, they did observe a sea-salt mass inversion generally just below cloud base. A negative vertical gradient of mass is to be expected, as most of the sea-salt mass lies in the larger super-micron sizes (Exton et al. 1985) which are unlikely to be well mixed throughout the boundary layer. It is for this reason that sea-salt has, in recent times, been excluded as a source of CCN (Charlson et al. 1987). However, measurements by Meszaros and Vissly (1974) and O’Dowd et al. (1997a) reported the existence of the sub-micron sea-salt mode, which dominates the sea-salt aerosol number concentration, but not the sea-salt mass. Thus, because these sub-micron sea-salt particles are similar in size to sulphate nuclei, they are equally likely to be well mixed throughout the boundary layer and up to cloud base.

Latham and Smith (1990) suggested that increases in global wind speeds may induce additional indirect radiative forcing, as more sea-salt nuclei are produced and mixed to cloud base. Whilst Latham and Smith suggested that sea-salt nuclei could contribute to the marine CCN population, their source functions for sea-salt nuclei only extended down to sizes of $0.5 \mu m$ radius. Later, O’Dowd and Smith (1993) further confirmed the existence of sea-salt nuclei down to sizes of $0.05 \mu m$, and illustrated that sea-salt nuclei in the size range $0.05$ to $0.5 \mu m$ were present in much higher concentrations than in the size range of $0.5$ to $1 \mu m$ reported by Latham and Smith; they argued that these sized particles can be readily mixed throughout the boundary layer up to cloud base. O’Dowd and Smith also showed that under certain clean air-mass conditions sea-salt dominated the marine aerosol accumulation mode, thus suggesting that sea-salt could not only provide a significant source of CCN, but also sometimes dominate the actual CCN population. Peak sea-salt concentrations were observed under conditions of high wind speeds and were observed to follow a power-law relationship dependent upon wind speed.

In this study, we present airborne measurements of marine sulphate and sea-salt nuclei and concentrations of cloud droplets over the north-east Atlantic and the north-east Pacific. Flights were undertaken during conditions when different source strengths of nss-sulphate and sea-salt CCN were dominant.

2. Instrumentation

The externally mixed secondary marine aerosol distribution is typically bi-modal (Hoppel et al. 1986), comprising an Aitken mode with typical mode radius of $\approx 30 \text{ nm}$ and an accumulation/cloud residual mode with a mode radius of $\approx 70$ to $100 \text{ nm}$ radius.
Aerosol–cloud droplet parametrization

A minimum in the size distribution is often observed at ≈50 nm and separates the Aitken and accumulation modes. The secondary accumulation mode is thought to result only from cloud processing of activated aerosol in which the dominant growth mechanism is the heterogeneous oxidation of aerosol precursors in solution (Hoppeletal. 1986). Thus, the concentration of secondary aerosol in the accumulation mode is thought to represent the concentration of activated, or actual, secondary CCN. Indeed, comparison of the sub-cloud aerosol distribution, the interstitial distribution, and cloud droplet spectra support this assumption (Hoppeletal. 1994). This secondary accumulation mode may also be viewed as the secondary aerosol–cloud residual mode, since it is only observed to occur in the presence of clouds (Hoppeletal. 1986; Hoppeletal. 1994; Kerminen and Wexler 1995). Since sea-salt aerosol particles larger than 50 nm are also readily activated into cloud droplets at supersaturations of less than 0.2% (Pruppachere and Klett 1978), the concentration of total aerosol larger than 50 nm can be considered to be representative of the concentration of nuclei which have acted as CCN in the marine atmosphere or, in other words, these sized particles are actual CCN.

Accumulation mode aerosol (radius 0.05 to 0.3 μm) measurements were taken using a Particle Measuring Systems (PMS) aerosol spectrometer probe ASASP-X optical particle counter mounted inside the Meteorological Research Flight C-130 research aircraft (this instrument covers radii 0.05 to 1.5 μm). An airborne volatility system was deployed to infer aerosol composition and its variation with size. The scanning-temperature volatility system previously used by O’Dowd and Smith (1993) required one-hour scanning periods, and thus was not suitable for airborne use. Instead, four heater tubes each set at a specific temperature were used: 40 °C to dry the ambient aerosol; 80 °C to volatilize methanesulphonic acid; 150 °C to volatilize sulphuric acid; and 350 °C to volatilize ammonium sulphate (O’Dowd etal. 1997b). Remaining aerosol at 350 °C was considered to be sea-salt aerosol in clean marine air. Whilst it is assumed that the aerosol remaining at 350 °C is sea-salt aerosol, it should be noted that recent work on super-micron marine aerosol has shown there to be a noticeable fraction of primary biological particles (<17%) present in the marine aerosol (Matthias-Maser etal. 1999). It is not clear whether these biological particles will be volatilized at temperatures below 350 °C or not, or whether they are present in similar fractions in the sub-micron aerosol. It should be noted also that a small fraction of externally mixed organic cloud residual aerosol has been observed in marine stratuscumulus, suggesting that some of these primary organic nuclei may also contribute to the cloud droplet population (Noone etal. 1999). Thus, use of this airborne volatility analyser allows reasonable differentiation between nss-sulphate and sea-salt cloud nuclei, and it has been used successfully by a number of investigators (Dinger etal. 1970; Clarke etal. 1987; Jenings and O’Dowd 1990). Supporting aerosol measurements were carried out by a wing-mounted Passive Cavity Aerosol Spectrometer Probe (PCASP) optical particle counter, whilst cloud droplet and sea-spray concentrations and size were measured by using a PMS Forward Scattering Spectrometer Probe (FSSP) optical particle counter.

3. Observations

Observations of cloud droplet and sub-cloud aerosol concentration are presented from 21 flights in stratuscumulus-covered marine boundary layers over the east Pacific and the north-east Atlantic. The north Atlantic flights (6 in total) were undertaken during winter, spring and summer from 1993 to 1995 under the UK Clouds Aerosol and Radiation programme; the east Pacific flights (15) were undertaken during the Monterey Area Ship Tracks (MAST) experiment and concentrated upon June 1994. Three of the north Atlantic flights were undertaken under wind speed conditions of 14 to 17 m s⁻¹, whilst the remaining
north Atlantic and east Pacific flights were conducted under more moderate wind speeds of 1 to 10 m s\(^{-1}\). A summary of the MAST experiment, and the conditions encountered for its duration can be found in Durkee et al. (1999).

(a) Cloud droplet–aerosol relationship

The relationship between sub-cloud aerosol (30 m below cloud base) and cloud droplet concentration (50 to 100 m below cloud top) for all flights is shown in Fig. 1. It is readily seen that this relationship is nonlinear, somewhat resembling a 1:1 relationship at low aerosol concentrations, but flattening off at higher sub-cloud aerosol concentrations. This behaviour is consistent with a lowering of the peak supersaturation achieved in clouds activated on high-concentration sub-cloud aerosol, resulting from more rapid depletion of water vapour as more larger nuclei become available as condensation sinks. The net effect of this is to increase the minimum size, and lower the number, of particles activated into droplets compared to those activated on a lower-concentration sub-cloud aerosol population for the same environmental conditions. The equation of the curve which provide the best fit to the data is:

\[
D = 197\{1 - \exp(-6.13 \times 10^{-3}A)\}
\]

where \(A\) (cm\(^{-3}\)) is the sub-cloud aerosol concentration and \(D\) (cm\(^{-3}\)) is the cloud droplet number concentration. There is little scatter observed in the dataset when compared to the fitted relationship; however, there are three cases for which this curve significantly over-predicts the observed droplet concentration (these points were not included in the curve fit). These three cases correspond to moderate to high wind speed conditions (14 to 17 m s\(^{-1}\)). In an attempt to understand why under high wind speeds the aerosol–droplet
relationship deviated from the relationship predicted for low wind speed conditions, a closer examination of aerosol properties under both high and low wind speed is conducted. Flight A334 (20 June 1994), 800 km off the west coast of California is chosen as a good low wind speed case (≈1 to 2 m s⁻¹) which provides very good agreement with the empirical parametrization above (see Fig. 1); Flight A320 (20 April 1994) about 500 km south-west of Mace Head, over the north Atlantic, is chosen as representative of the highest wind speeds encountered (17 m s⁻¹) and resulted in the poorest agreement with the parametrization.

(b) Pacific maritime: low wind speed (Flight A334)

Figure 2 displays the observed aerosol and cloud droplet concentrations over a profile through the marine boundary layer approximately 500 km off the Californian coast. The boundary-layer depth was 900 m and it was capped by a shallow stratocumulus cloud deck approximately 150 m deep. Sub-cloud aerosol concentrations were ≈90 cm⁻³ whilst cloud droplet concentrations were ≈80 cm⁻³, indicating that nearly 90% of the aerosol were active as CCN. Using the volatility technique we were able to separate the nss-sulphate and sea-salt distributions and examine the relative contribution of each aerosol species to the CCN population.

Nss-sulphate and sea-salt size distributions, observed on the same flight but at a distance of 600 km off the coast are shown in Fig. 3. The sulphate contribution to the total accumulation mode aerosol concentration (N = 71 cm⁻³) was 90%, whilst the remainder was attributed to sea-salt aerosol. The reduction in the aerosol concentration compared to the concentration at 500 km is thought to be due to the increase in boundary-layer height, and thus mixing volume, as one moves further off the coast. Although the larger sea-salt nuclei will be activated first into cloud droplets, it is clear than the majority (≈90%) of the cloud droplets would have been formed on nss-sulphate aerosol. This is not surprising since no white-caps were observed during this flight, and thus sea-salt CCN production was at a minimum. For most cases where wind speeds were 10 m s⁻¹ or less, the majority of cloud droplets were formed upon sulphate nuclei.
(c) Atlantic maritime: high wind speed (Flight A320)

The highest wind speeds (≈17 m s⁻¹) encountered during the Atlantic maritime series of flights were to the west of the Irish coast over the north-east Atlantic. Air mass back trajectories indicated a tropical maritime history for this air mass. The maritime nature of this air mass was corroborated by observations of typically maritime soot carbon mass loadings (20 ng m⁻³) upwind and, in the same air mass, at the Mace Head background-monitoring station on the Irish coast. The vertical distribution of aerosol and cloud droplets is shown in Fig. 4. The boundary layer was decoupled, with a surface layer 600 m in depth which contained a solid stratocumulus cloud deck approximately 300 m thick. The decoupled layer, extending from 600 m to 1500 m, contained a very shallow dissipating cloud of about 50 m in thickness. We should note that the PCASP measurements in cloud are removed due to droplet shattering effects.

In the surface layer, sub-cloud aerosol concentrations were well mixed from the surface to cloud base and averaged ≈250 cm⁻³, however, the cloud droplet concentration observed was a very modest 50 cm⁻³, and thus the ratio of cloud droplets to sub-cloud aerosol was considerably less than that observed under low to moderate wind speed conditions. Volatility analysis of the aerosol indicated that the contributions of nss-sulphate and sea-salt aerosol to the sub-cloud aerosol were 167 cm⁻³ and 72 cm⁻³, respectively. It should be noted that both the nss-sulphate and sea-salt aerosol in the surface layer were well mixed up to cloud base. The nss-sulphate and sea-salt size distributions taken just below cloud base are shown in Fig. 5. Nss-sulphate aerosol possessed a mode radius of 0.078 μm and dominated the concentration at sizes smaller than 0.1 μm radius, whilst sea-salt aerosol dominated the aerosol concentration at larger sizes.

The larger sizes associated with sea-salt aerosol compared with those of nss-sulphate, combined with the lower activation threshold required to activate sea-salt nuclei of a similar size, suggests that the sea-salt nuclei would be activated first, and in preference to nss-sulphate nuclei, during the early stages of cloud formation (Pruppacher and Klett 1978).
Figure 4. Vertical profiles of observed aerosol and cloud droplet concentrations (cm\(^{-3}\)) for the north-east Atlantic high wind speed case (Flight A320).

Figure 5. Nss-sulphate and sea-salt size (radius \(r, \mu m\)) distributions (concentration \(N, \text{cm}^{-3}\)) observed for high wind speed Atlantic maritime aerosol (Flight A320). See text for details.

(d) Influence of sea-salt on CCN activation

In comparison with the above, the most striking difference between cases is observed in the increase in sea-salt concentration relative to the sulphate concentration, particularly at the larger sizes, with the ratio of sulphate to sea-salt concentration decreasing from \(\approx 8\) in the low wind speed case to 2.3 in the high wind speed case. It appears that this change in ratio can lead to significant changes in the activation processes during cloud formation, which are most likely to result from the initial activation of sea-salt nuclei. To
examine the fraction of sea-salt nuclei activated into cloud droplets (for the high wind speed Atlantic case) we can use a one-dimension (1-D) Lagrangian rising-parcel cloud model (Pruppacher and Klett 1978) to predict, by inserting the measured aerosol distributions, the supersaturation reached in the cloud which will activate the observed cloud droplet concentration of 50 cm\(^{-3}\). The physical aspects of the simulation consists of a Lagrangian parcel model with explicit particle micro-physics. The micro-physical aspect utilizes the droplet nucleation and dynamic-growth equations (Pruppacher and Klett 1978) to model the activation and growth of aerosol solution droplets by the condensation of water vapour onto a size-resolved aerosol spectrum of up to 100 size-resolved droplet classes. Rather than being fixed, the boundaries of these size channels move as the solution droplets grow. The growth law includes curvature and solution effects, and is corrected for the breakdown of the continuum approximation close to the droplet surface (Pruppacher and Klett 1978). Entrainment processes are not included in this model.

By inputting the separate sea-salt and nss-sulphate distributions, we can also infer the fraction of activated cloud droplets formed on sea-salt and sulphate nuclei. The measured nss-sulphate distribution was found to resemble a log-normal (to base 10) curve possessing the following parameters: \(N_{\text{nss-s}} = 167 \text{ cm}^{-3}\); \(r_g = 0.078 \mu m\); and \(\sigma = 1.27\) where \(N_{\text{nss-s}}\) is the concentration, \(r_g\) is the dry mode radius of the distribution, and \(\sigma\) is the standard deviation as defined in Seinfeld and Pandis (1998). The film-drop sea-salt aerosol distribution (radius 0.05–0.5 \(\mu\)m) observed using this optical particle counter is, however, affected by multiple (Mie) scattering response artefacts, resulting in some oversizing of the sub-micron sea-salt aerosol (at sizes around 0.1 \(\mu\)m) and the appearance of an artificial ‘bump’ in the sea-salt spectrum at approximately 0.1 to 0.2 \(\mu\)m. Rather than applying a scattering-response correction to overcome this effect, we use the film-drop log-normal distributions reported in O’Dowd et al. (1997a) and scale this distribution to the concentration observed here. This approach leads to: \(r_g = 0.1 \mu m\), \(\sigma = 1.9\), and concentration \(N = 72 \text{ cm}^{-3}\). The larger jet-drop sea-salt mode (O’Dowd et al. 1997a) must also be included in the calculations; the log-normal parameters for this mode, under these conditions, are: \(N = 3.5 \text{ cm}^{-3}\), \(r_g = 1 \mu m\), and \(\sigma = 2\).

The CCN supersaturation spectrum derived from the parcel-model simulations is shown in Fig. 6 which illustrates that 50 cm\(^{-3}\) droplets are activated at a supersaturation of \(\approx 0.045\%\). At this supersaturation, \(\approx 80\%\) of the cloud droplets are activated on sea-salt nuclei. Such a low supersaturation is brought about by the presence of the more active, and larger sized, sea-salt nuclei which are activated at supersaturations considerably lower than that required to activate nss-sulphate nuclei. The activation of these nuclei in the initial stages of cloud nucleation tends to consume water vapour at low supersaturations, and thus suppresses the peak supersaturation achieved within the cloud. To illustrate the impact of the sea-salt spectrum on droplet nucleation and peak supersaturation, we can compare these simulations with others initialized without sea-salt nuclei. The same modelling experiment as before is repeated (i.e. same conditions and same range of updraughts), however, this simulation contained only the sulphate spectrum. Figure 7 displays the constructed CCN supersaturation spectrum for these simulations. The same updraught required to activate the observed 50 cm\(^{-3}\) droplets in the previous simulation now results in a higher peak supersaturation of 0.121\%, leading to an increase in the activated CCN droplets from 50 cm\(^{-3}\) to 149 cm\(^{-3}\). It should be highlighted that this predicted droplet concentration for a sulphate-only aerosol population agrees very well with the fitted empirical relationship derived in Fig. 1 for low wind speed and low sea-salt conditions. Thus, the addition of 72 cm\(^{-3}\) sea-salt nuclei to an existing sulphate CCN population of 169 cm\(^{-3}\) results in a decrease in the cloud droplet concentration from 149 cm\(^{-3}\) to 50 cm\(^{-3}\). These results illustrate the importance of knowing CCN size and composition when considering the
Figure 6. Calculated sea-salt and total (sulphate and sea-salt) supersaturation spectra for north-east Atlantic high wind speed case (Flight A320).

Figure 7. Calculated nss-sulphate CCN supersaturation spectrum for north-east Atlantic high wind speed case with sea-salt aerosol removed. See text for details.
impact of increased CCN concentrations on cloud micro-physics. It is also suggested that, to predict accurately the effect that increased sulphate CCN concentrations will have on cloud droplet concentration, and thus radiative forcing, the presence of other sources of CCN, particularly sea-salt, must be taken into account.

4. PARAMETRIZATION FOR MULTI-COMPONENT AEROSOL–DROPLET RELATIONSHIPS

(a) Current and past parametrization

In order to represent the indirect effect of aerosol on radiative forcing in computationally intensive general circulation models (GCMs), a simple relationship between sub-cloud aerosol and cloud droplet concentration is required. However, the relationship between cloud droplet concentration and aerosol concentration is a complex and dynamic feedback function of aerosol size, aerosol chemistry, vertical updraught, and peak supersaturation. This complexity is further compounded by the presence of a multi-component aerosol size distribution, as previously illustrated. Early attempts to relate cloud micro-physical properties to sub-cloud aerosol or, more specifically, the sub-cloud CCN supersaturation spectrum, were conducted by Twomey (1959) and Squires (1958). In these studies, cloud droplet concentrations were derived using approximations of the droplet activation and growth formula applied to a CCN supersaturation spectrum. The form of the supersaturation spectrum used was based on the empirical relationship:

\[ N = c(100 + S^*)^k, \]  

where \( c \) (cm\(^{-3}\)) is proportional to the CCN concentration at 1% supersaturation, \( k \) is the slope parameter of the CCN size spectrum, and \( N \) (cm\(^{-3}\)) is the number of nuclei activated into cloud droplets at peak supersaturation \( S^* \). Values of \( c \) and \( k \) are normally derived from measurements of the CCN supersaturation spectrum, and are dependent on aerosol (or CCN) source strengths, sizes and concentrations. Feingold and Heymsfield (1992) developed more rigorous parametrizations, although still approximations, of the nucleation and growth formula; these included, for example, kinetic effects omitted from the Twomey (1959) parametrization. The study by Feingold and Heymsfield (1992) explored the accuracy of the two aforementioned parametrizations through comparison with predicted droplet concentration and effective radius from a detailed micro-physical model, and found reasonable agreement between all schemes. For example, the Feingold and Heymsfield scheme for moderate updraughts (0.5 m s\(^{-1}\)) predicted \( N \) and \( S^* \) to within 20% of the micro-physical-model predictions for most values of \( c \) and \( k \), whilst the Twomey scheme over-predicted by a factor of 2 for small \( k \) and high \( c \) values. For simulations of high updraught velocities (1 m s\(^{-1}\)), both schemes displayed improved performance.

The approach of using CCN relationship (2) as input to both parametrization schemes and micro-physical models has conventionally been used in the past, however, there are some shortcomings and limitations to using this method. Feingold and Heymsfield (1992) point out that this representation constrains the CCN spectrum to a simple power-law representation which may not always be realistic. In fact, since the CCN spectrum comprises contributions from many aerosol modes (sea-salt film mode, sea-salt jet-drop mode and accumulation mode sulphate nuclei) it is unlikely that this simple representation can capture nonlinearities in the actual CCN supersaturation spectrum. Further, use of this representation has been based on using 'typical' values of \( c \) and \( k \) for different environmental conditions (e.g. continental and maritime air masses) and are not, as such, directly related to prognostic variables available in GCMs.
As GCMs become more sophisticated, it is necessary to try to predict indirect radiative forcing from specific aerosol species; chemical-transport models are often run alongside, or coupled to, the GCM in order to provide grid-sector aerosol chemical mass which can then be converted to either an aerosol or CCN spectrum. With the recent intense focus on radiative forcing by sulphate aerosols, new aerosol–droplet parametrization schemes have been explored, primarily in a semi-empirical manner (Hegg 1984; Boucher and Lohmann 1995; Jones et al. 1994). Hegg, using airborne data, related CCN concentration active at a supersaturation of 1% to total sulphate mass, and found the following relationship:

\[ N_{CCN} = 90.7m^{0.45} + 23, \]  

(3)

where \( m \) (kg) is the mass of aerosol sulphate. Boucher and Lohmann, in a similar manner, and using a variety of dataset sources, related sulphate mass to CCN concentration in the form:

\[ N_{CCN} = 10^{2.21+0.41 \log(m)}. \]  

(4)

In both of these schemes, the number of CCN is considered to equate to the number of activated cloud droplets. These approaches, which relate sulphate mass to CCN active at a certain supersaturation, are subject to errors as there is not necessarily a direct relationship between sulphate mass and CCN. Further, incorrect assumptions are made concerning the supersaturation, as no dynamic feedback between activation of nuclei and supersaturation suppression is incorporated into this approach. The usefulness of a relationship between CCN, active at 1%, and sulphate mass is somewhat limited since CCN active at this supersaturation are unlikely to contribute much to the marine stratocumulus cloud droplet population (which are activated at \( \approx 0.2\% \) supersaturation).

The approach employed by Jones et al. (1994) is an improvement on the sulphate-mass CCN approach since actual measured cloud droplet concentration is used in the parametrization development. Using aircraft observations (Martin et al. 1994) of sub-cloud accumulation mode aerosol and cloud droplet concentration, Jones et al. found the following relationship:

\[ N_{CD} = 375\{1 - \exp(-2.5 \times 10^{-3}A)\}, \]  

(5)

where \( N_{CD}(\text{cm}^{-3}) \) is the cloud droplet concentration. This empirical parametrization was then used in conjunction with a chemical-transport model to translate sulphate mass to a cloud droplet relationship, by allocating all sulphate mass to a log-normal accumulation mode aerosol distribution, with a mode radius of 50 nm, and then predicting cloud droplet concentration from the accumulation mode concentration. Clearly there are some shortcomings to this approach; in assuming that all sulphate mass is present in the accumulation mode, one overlooks the fact that in the marine environment a significant amount, if not the majority, of sulphate mass can be internally mixed with sea-salt aerosol, and thus does not contribute to CCN enhancement (Sievering et al. 1992; O’Dowd et al. 1997a, 1999). Further, this approach cannot capture the effects of including multiple CCN sources as discussed in the previous section.

In Fig. 8 the empirically derived relationships from Jones et al. (1994) Boucher and Lohmann (1995) and Hegg (1984) are compared to the observed relationship found in this study. In this comparison, the Boucher and Lohmann and the Hegg parametrizations are converted from sulphate mass to aerosol concentration by assuming that all the sulphate mass contributes to a log-normal aerosol-sulphate distribution with mode radius of 75 nm and standard deviation of 1.4. Excellent agreement can be seen between this study and that of Jones et al. for sub-cloud aerosol concentrations of less than 250 cm\(^{-3}\). Above this
Fig. 8. Comparison of empirically derived aerosol–cloud droplet relationships from: this study; Jones et al. (1994); Hegg (1984); and Boucher and Lohmann (1995). See text for discussion.

concentration the Jones et al. curve over-predicts the droplet concentration compared with this study. We should note that there are some differences between these two empirical data sets: the Jones et al. relationship covers primarily maritime clouds for the lower aerosol-concentration regime and continental clouds for the higher aerosol concentrations, whilst all data leading to the relationship derived in this study relate to marine clouds. It is possible that the deviation results from generally stronger updraughts associated with continental clouds, leading to an increase in the number of activated droplets for a given sub-cloud aerosol concentration. Neither the Hegg nor the Boucher and Lohmann CCN–sulphate mass relationships compare well to the measured aerosol–droplet relationships, particularly at low particle concentration. For the lowest aerosol concentration, cloud droplet concentration is greatly over-predicted by a factor of 2 to 5; however, at higher concentrations the Boucher and Lohmann relationship displays better agreement with that of Jones et al., while the Hegg relationship displays improved agreement with this study. It should be noted that this large error in the sulphate mass–CCN schemes occurs for the most susceptible region in the aerosol–cloud system, where both schemes greatly over-predict the number of cloud droplets in the cleanest environments. Whilst the empirical relationships derived in both this study and that of Jones et al. appear to be applicable in most cases under low to moderate wind speeds, neither can be used to predict droplet concentration under conditions where sea-salt nuclei contribute significantly to cloud formation. A more sophisticated aerosol–droplet parametrization which encapsulates the physical processes governing cloud activation on a multi-component aerosol population is required for use in GCMs.

(b) Multi-component parametrization development

In an attempt to take account of some of these dynamic aerosol–droplet effects for a combined sea-salt and sulphate aerosol population, parametrizations of the relationship
between droplet concentration and a multi-component aerosol system are developed using the micro-physical cloud model mentioned earlier. Wind speed, a surrogate for sea-salt concentration, can be used as a variable since it is typically already available in a GCM. In developing these parametrizations, model simulations similar to those previously described were conducted over a wide range of environmental conditions and aerosol concentrations. As discussed and illustrated earlier, marine cloud nuclei are composed primarily of nss-sulphate and sea-salt aerosol. The representations of these two aerosol species were based on observations from many different marine locations. Nss-sulphate aerosol, in these simulations, is represented by a log-normal distribution with \( r_g = 0.075 \mu \text{m} \) and \( \sigma = 1.4 \) (O'Dowd et al. 1993). Sea-salt nuclei are characterized by two log-normal distributions corresponding to the film and jet drop modes (O'Dowd et al. 1997a). The film drop mode possesses log-normal parameters \( r_g = 0.1 \mu \text{m} \) and \( \sigma = 1.9 \), whilst the jet-drop mode is described with parameters \( r_g = 1 \mu \text{m} \) and \( \sigma = 2 \) (O'Dowd et al. 1997a). The multi-component aerosol distributions are used as input to the Lagrangian parcel model along with initial, typical, boundary-layer conditions and parcel updraughts. Initially, simulations of cloud formation were performed with parcel updraughts of 0.1, 0.15, 0.175, 0.2 and 1 m s\(^{-1}\) and sulphate concentrations varying from 0 to 600 cm\(^{-3}\). Sea-salt concentrations were determined from the 10 m wind speed relationship reported in (O'Dowd et al. 1997a) which was varied from 2 m s\(^{-1}\) to 16 m s\(^{-1}\) in 2 m s\(^{-1}\) increments.

The simulation results for 0.175 m s\(^{-1}\) updraughts were found to most closely predict, with very good agreement, the Jones et al. (1994) parametrization and the empirical parametrization from this study, and thus are studied in more detail alongside the simulation results for the 0.1 m s\(^{-1}\) updraughts. For these two simulation scenarios, parametrizations were developed from multiple simulations, leading to the following aerosol–droplet relationship:

\[
D = A_1 \left(1 - e^{A_2 U}\right).
\]  

(6)

The parameters \( A_1 \) and \( A_2 \) are derived for each updraught and are functions of wind speed \((U; \text{m s}^{-1})\). Thus, this treatment leads to a representation of droplet concentration as a function of sulphate concentration, \( U \) and sea-salt. In the case of a 0.1 m s\(^{-1}\) updraught, the values of \( A_1 \) and \( A_2 \) were found to be:

\[
A_1 = 225.7 - 1.909 U - 0.164 U^2
\]

(7)

\[
A_2 = \frac{(3.327 - 0.00682 U + 0.0051 U^2)}{1000},
\]

and for the 0.175 m s\(^{-1}\) updraught case, these parameters were:

\[
A_1 = 365.16 - 2.038 U - 0.438 U^2
\]

(8)

\[
A_2 = \frac{(2.481 - 0.04922 U + 0.00527 U^2)}{1000}.
\]

In Fig. 9, the excellent agreement between the micro-physical-model simulation results and the parametrized aerosol–droplet relationship is illustrated for the 0.175 m s\(^{-1}\) vertical updraught and 8 m s\(^{-1}\) wind speed; this suggests that this parametrization can be used with some degree of confidence. Also, excellent agreement between the parametrized coefficients \( A_1 \) and \( A_2 \) and the micro-physical-simulation results can be seen in Fig. 10.
The behaviour of this aerosol–droplet parametrization for the selected updraught velocities of 0.1 and 0.175 m s\(^{-1}\) and selected wind speeds of 2, 8, 14 and 18 m s\(^{-1}\), is illustrated in Fig. 11. For low aerosol concentrations, as observed with the measured data, the relationship is approximately linear; for larger aerosol concentrations, the gradient of the relationship reduces, particularly for the lower strength updraught. The effect of increasing wind speed, and thus increasing sea-salt nuclei concentration, is readily seen to reduce the cloud droplet concentrations, particularly at moderate to high aerosol concentrations. The result of enhancing sea-salt concentrations is to produce a flattening of the aerosol–droplet relationship curve, and a concomitant lowering of the absolute magnitude of the relationship—similar to the effect observed in the measurements under high wind conditions. For the stronger updraught case, the rate of cooling of the air parcel increases, and thus tends to increase the peak supersaturation reached in cloud. This increase in peak supersaturation allows activation of smaller nss-sulphate aerosol, which would otherwise not be activated at the lower supersaturations achieved for the lower velocity updraught case; consequently, relative to the lower velocity updraught case, this results in an increase in the concentration of cloud droplets for a given sub-cloud aerosol concentration.

It is also useful to examine the predicted cloud droplet concentration as a function of sulphate nuclei concentration and wind speed. The behaviour of the parametrization for the 0.1 and 0.175 m s\(^{-1}\) updraught scenarios, for different wind speed conditions is illustrated in Fig. 12. For low sulphate concentrations and increasing wind speed, the predicted cloud droplet concentration increases as more sea-salt nuclei become available and dominate the cloud nucleation processes. For high sulphate concentrations, the produced cloud droplet concentration is reduced significantly as wind speed increases, primarily due to the suppression of the peak supersaturation reached in cloud. In these sulphate versus cloud droplet curves, it is clearly seen that as updraught (and thus supersaturation) is reduced, the concentration of sulphate nuclei at which the presence of sea-salt switches from reducing to increasing the droplet concentration also reduces.
Figure 10. Variation of coefficients $A_1$ and $A_2$ as a function of wind speed. Also shown are the parametrized coefficients as a function of wind speed. See Eq. (6) and discussion.

Figure 11. Predicted cloud droplet concentrations as a function of sub-cloud aerosol concentration (combined sea-salt and sulphate aerosol) and wind speed ($U$) for 0.1 and 0.175 m s$^{-1}$ updraughts.
In Fig. 13, the parametrizations for the 0.175 m s$^{-1}$ updraught at 2, 8, 12, 18 m s$^{-1}$ wind speeds are compared to the empirical relationships reported in this study and the Jones et al. (1994) study. For the purposes of the comparison, the parametrized relationships for a very high updraught speed of 1 m s$^{-1}$ and low updraught speed of 0.1 m s$^{-1}$ at a wind speed of 8 m s$^{-1}$ are also included. Clearly, very good agreement is observed between the experimental empirical curves and the parametrizations curves at the 0.175 m s$^{-1}$ updraught scenario. For a given wind speed, the effect of reducing the updraught to 0.1 m s$^{-1}$ is to reduce the predicted cloud droplet concentration at all sub-cloud aerosol concentrations, while increasing the updraught to 1 m s$^{-1}$ provides the largest deviation from the experimental data primarily for the highest aerosol concentrations. The derived aerosol-droplet relationships, as stated earlier, agree quite well with the measurements shown in this work and those from Martin et al. (1994) and Jones et al. (1994); they also provide better agreement than the approaches using sulphate mass–CCN schemes. Although there is some scatter in both sets of data (Martin et al. and this study), this is not unexpected and is significantly less that the scatter seen in the sulphate mass–CCN datasets. Both aerosol and cloud drop datasets were gathered over a wide variety of meteorological conditions under which actual updraught, and thus peak supersaturation in cloud was likely to vary considerably. Consequently, the reported curve-fits in the two datasets are considered representative of ranges of environmental conditions and average updraught velocities.

Although the trend of decreasing droplet concentration as a function of increasing sea-salt concentration, seen in the measurements database, is replicated quite well in the model-derived relationship, this relationship does not reproduce droplet concentrations as low as those observed in the high wind speed cases (Flight A320) shown in Fig. 1. Whilst very low updraughts (0.05 m s$^{-1}$) can reproduce this effect, these updraughts are probably too slow to be realistic. The most likely explanation for the model simulations not being able to reproduce the high wind speed case-study (Flight A320) droplet concentration at the 0.1 m s$^{-1}$ updraught, is that the sea-salt nuclei were partially internally mixed with less-soluble species such as organic aerosol (Noone et al. 1999). The presence of less-soluble internally mixed species will tend to lower the number of aerosol activated for a given supersaturation. Finally, we must stress that the model used here is a simple micro-
Figure 13. Comparison of predicted cloud droplet concentrations for parametrized sub-cloud aerosol and empirically derived relationships. Parametrized results are shown for wind speeds 2, 8, 12, and 18 m s⁻¹ for 0.175 m s⁻¹ updraughts (U), and 8 m s⁻¹ wind speeds for 1 and 0.1 m s⁻¹ updraughts. Also shown are the empirical parametrizations derived from this study and from Jones et al. (1994).

physical parcel model and lacks the complexity and detail often found in more advanced models. Nevertheless, these simulations highlight the importance of accounting for multi-component aerosol species in the cloud formation process, and provides an improved, more realistic, and simple approach for inclusion of multi-component aerosol species into large-scale models. Future work should be dedicated to further refining the aerosol–droplet parametrization by the addition of an updraught velocity variable, variable mode radii, and more realistic aerosol species such as internally and externally mixed organic species. Such improvements will greatly increase model complexity.

The net effects of inclusion of a second source of cloud nuclei, other than nss-sulphate, are: to reduce the fraction of sulphate nuclei activated into cloud droplets; to increase droplet concentration for clean, low sulphate, conditions; and to decrease the droplet concentration for more polluted, higher sulphate, conditions. A reduction in the fraction of cloud droplets activated on sulphate nuclei suggests that any indirect climate forcing by sulphate aerosols may be reduced somewhat in the presence of other nuclei.

5. Conclusions

In clean maritime conditions with low wind speeds, nss-sulphate aerosol dominates the CCN population, and thus is responsible for most of the activation of cloud droplets. The relationship between sub-cloud aerosol and cloud droplet concentration is found to be nonlinear, in agreement with other studies, and follows (1). In the presence of other CCN sources, such as sea-salt under moderate to high wind speed conditions, this (and other) relationships significantly over-predict the observed droplet concentration by up to 100% or more, and is not applicable for general use. Using observed sea-salt and nss-sulphate aerosol size distributions combined with a simple cloud model, it is inferred that
approximately 80% of the cloud droplets can be formed upon sea-salt nuclei, even under sulphate-rich conditions. The reason for the over-prediction of cloud droplet concentration for a given sub-cloud aerosol concentration, under moderate-to-high wind speed conditions, is the preferential activation of larger, more active, sea-salt nuclei concomitant with a suppression of the peak supersaturation reached in the cloud.

A new aerosol–droplet parametrization has been developed which determines the cloud droplet concentration as a function of both sulphate and sea-salt aerosol concentrations for different updraught velocities. This parametrization closely agrees with observations from the north Atlantic and east Pacific, and is suitable for use in GCMs. The behaviour of this parametrization illustrates that the addition of sea-salt nuclei to the sulphate CCN population reduces the total number of cloud droplets activated in more polluted conditions, and increases the number of droplets under cleaner conditions. The effect of including an additional source of marine CCN is to reduce the impact of nss-sulphate nuclei on cloud droplet concentrations, and thus is likely to reduce the predicted sulphate aerosol indirect radiative forcing effect.

ACKNOWLEDGEMENTS

This work was supported by the Natural Environment Research Council under contracts GST/02/659 and GR3/9416. The authors would like to thank the aircrew of the C-130 and the support staff at the Meteorological Research Flight, DRA, Farnborough.

REFERENCES


Matthias-Maser, S., Brinkmann, J. and Schneider, W. 1999 The size distribution of marine atmospheric aerosol in consideration of primary biological aerosol particles over the South Atlantic Ocean. *Atmos. Environ.*, in press


