Integrating biomass, sulphate and sea-salt aerosol responses into a microphysical chemical parcel model: implications for climate studies

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Aerosols are known to influence significantly the radiative budget of the Earth. Although the direct effect (whereby aerosols scatter and absorb solar and thermal infrared radiation) has a large perturbing influence on the radiation budget, the indirect effect (whereby aerosols modify the microphysical and hence the radiative properties and amounts of clouds) poses a greater challenge to climate modellers. This is because aerosols undergo chemical and physical changes while in the atmosphere, notably within clouds, and are removed largely by precipitation. The way in which aerosols are processed by clouds depends on the type, abundance and the mixing state of the aerosols concerned. A parametrization with sulphate and sea-salt aerosol has been successfully integrated within the Hadley Centre general circulation model (GCM). The results of this combined parametrization indicate a significantly reduced role, compared with previous estimates, for sulphate aerosol in cloud droplet nucleation and, consequently, in indirect radiative forcing. However, in this bicomponent system, the cloud droplet number concentration, $N_d$ (a crucial parameter that is used in GCMs for radiative transfer calculations), is a smoothly varying function of the sulphate aerosol loading. Apart from sea-salt and sulphate aerosol particles, biomass aerosol particles are also present widely in the troposphere. We find that biomass smoke can significantly perturb the activation and growth of both sulphate and sea-salt particles. For a fixed salt loading, $N_d$ increases linearly with modest increases in sulphate and smoke masses, but significant nonlinearities are observed at higher non-sea-salt mass loadings. This non-intuitive $N_d$ variation poses a fresh challenge to climate modellers.

Keywords: aerosol; clouds; climate; biomass; sulphate

1. Introduction

Recent research on the impact of natural and anthropogenic aerosols on global climate indicates that sulphate aerosol particles mainly have a cooling effect because they are effective reflectors of solar radiation and absorb very little of the incident radiation. Estimates of the aerosol direct effect on climate vary but global averages are generally between 0 and $-1 \text{ W m}^{-2}$ for present-day

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conditions (IPCC 2001). Since aerosols have short lifetimes (approx. a few days), their radiative forcing tends to peak and localize close to source regions. Although the most prominent source regions are Europe, North America and Southeast Asia, certain parts of central Africa and South America are also strong source regions of aerosol particles due to increased biomass burning. Although the probable impact of sulphate aerosol on climate has recently been studied (IPCC), the impact of biomass aerosol had not received much attention until large-scale campaigns such as ACE-Asia and INDOEX were launched.

Biomass burning makes a significant contribution to atmospheric trace gases and aerosol particles on both local and global scales. Andreae et al. (1996) have estimated that biomass burning could be responsible for as much as 45% of the global emissions of black carbon, which is an efficient absorber of solar radiation. Second, smoke particles can also act as cloud condensation nuclei (CCN). It was observed that 80–100% of the particles emitted during vegetation fires in California could act as CCN (Rogers et al. 1991). Cloud reflectivity is changed in the presence of biomass burning and the subsequent release of aerosol particles, causing changes in the albedo of tropical regions during the biomass burning season. Roberts et al. (2003) found that, in the Amazon basin during the dry season, smoke aerosol from biomass burning dramatically increased CCN concentrations. Furthermore, they found that light-absorbing substances in smoke darken the Amazonian clouds and reduce the net radiative forcing. A comparison of the advanced very high resolution radiometer analysis and their modelling studies suggests that the absorption of sunlight due to smoke aerosol may compensate for about half of the maximum aerosol effect. In accordance with our own study, they also found that subtle differences in the chemical and physical make-up are particularly influential in the activation and growth behaviour of the aerosol. They further concluded that knowledge of the CCN spectrum alone is not sufficient to fully capture the climatic influence of biomass burning.

A significant improvement in model studies was achieved when the importance of sea salt within an air mass comprising sulphate aerosol particles was recognized (Smith et al. 1996; O’Dowd et al. 1999a,b; Jones et al. 2001). It was found that, when a second aerosol such as sea salt is included, it has the potential to perturb the droplet activation process. The resultant values of $N_d$ varied notably when sea-salt aerosol particles were included. 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 bicomponent aerosol–droplet parametrization for use in general circulation models (GCMs) was developed to predict cloud droplet number concentration as a function of sea-salt and non-sea-salt sulphate nuclei. These studies demonstrated that the effect of enhancing an existing non-sea-salt sulphate CCN population with sea-salt nuclei is to reduce the number of cloud droplets activated under high sulphate conditions and to increase the cloud droplet concentration when sulphate levels are low. Ghan et al. (1998) also showed that the total number concentration of activated cloud droplets increases with increasing sea-salt concentration if sulphate number concentrations are relatively low and updraughts are strong, but it decreases with higher sea salt if sulphate number concentrations are high and cloud updraughts are weak. This is due to the activation of accumulation mode sea-salt particles, while the decrease arises
from the reduction in maximum cloud supersaturation due to competition with coarse mode sea-salt particles. These conclusions are insensitive to sulphate size distribution and surface wind speed.

Modellers now recognize the fact that aerosol activation and cloud processing effects are complex and should be effectively integrated within global aerosol-climate model studies (Roelofs et al. 2006). In a recent study, Fountoukis & Nenes (2005) have developed parametrizations to include sulphate and sea-salt aerosol. Their formulation allows for a lognormal representation of aerosol size distribution and includes a size-dependent mass accommodation of water vapour. However, no studies have been reported to date where the aerosol activation process has been examined when three components, i.e. sulphate, sea-salt and biomass aerosols, are included. In this study, we have examined in detail the modulation of the activation process when multiple aerosol components (more representative of a real atmosphere) are present. For the first time, we have studied with repeated model runs how $N_d$ varies with various mass loadings of the three components.

2. An overview of the microphysical chemical parcel model

A detailed microphysical chemical parcel model was the main tool used (O’Dowd et al. 1999a). The original model could account for only pure externally mixed sulphate and sea-salt aerosols. This model was updated and altered to include biomass smoke particles, which were assumed to be internally mixed with sulphate aerosol material.

The chemical model used is, in essence, a Lagrangian parcel model with explicit microphysics using the dynamic growth equation (Pruppacher & Klett 1997) to model the growth of aerosol solution droplets by condensation of water vapour onto a size-resolved droplet spectrum. 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 & Klett 1997). Mass transport limitations based on Schwartz (1986) have also been included. The aqueous-phase chemical aspects of the model consist of (i) an equilibrium module, (ii) a kinetic reaction module, and (iii) the non-ideal behaviour correction module (Pitzer 1991). The equilibrium module is used to calculate the amount of soluble gaseous species dissolved in the aerosol, and to apportion the aqueous aerosol species between the various associated and dissociated forms, which is achieved by solving the charge balance equation for each droplet. Although there are a number of similar models in existence, the present Pitzer model is one of the most advanced of its kind. Apart from including all the standard features of droplet growth considered by all microphysical models, it also takes account of high ionic strength, non-ideal solution effects. These effects impact aqueous-phase chemical equilibria via Henry’s law.

The kinetic reaction module is used to compute the rate of heterogeneous sulphate production in the solution droplets and sulphate production is allowed to occur by SO$_2$ oxidation using dissolved H$_2$O$_2$ and/or O$_3$ as the oxidant. The reaction rates and their temperature dependence are taken from Ayers & Larson (1990). Sources of atmospheric sulphur are dimethyl sulphide in the ocean and gaseous SO$_2$ from anthropogenic emissions, as well as from biomass smoke.
These species are quickly transformed to sulphate, in either the nucleation or the accumulation mode (Seland & Iversen 1999). Some of the nucleation mode particles coagulate on pre-existing background aerosol to form accumulation mode particles so important to the aerosol indirect effect. The second contribution to accumulation mode sulphate comes from SO$_2$ oxidation in clouds followed by evaporation, and recent sensitivity tests have shown this latter sulphate component to be more effective than the former as far as the second indirect effect is concerned (Seland & Iversen 1999). For these reasons, it was very important to include the kinetic reaction module in our model simulations. Further details of the model can be found in O’Dowd et al. (1999a).

3. Model performance and testing: consolidation of observational studies from ACE-2

Prior to configuring the microphysical model for multiple components, it was necessary to first assess the model performance with just ammonium sulphate and sea salt. The rationale behind this approach is twofold: first, the performance of the chemical parcel model could be tested with observational data from ACE-2 (aerosol characterization experiment) and, second, the biomass aerosol signature on the cloud optical properties could be singled out from model runs. ACE-2 measurements were also used to initialize the model, because the data pertain to stratocumulus clouds that contribute significantly to the aerosol indirect effect owing to their extensive coverage. We have used results for the C-130 flight A550 (25 June 1997) corresponding to a clean air mass for our base runs and thereafter simulated the biomass smoke effects as an added component.

First, we examined the accuracy of the heterogeneous cloud processing by comparing the masses of SO$_2^{-}$ and NH$_4^{+}$ in the fine mode. The modelled values for SO$_2^{-}$ and NH$_4^{+}$ are 0.069 and 0.150 ppb compared with the observed values of 0.109 and 0.157 ppb, respectively, for the two ionic species. Allowing for the experimental errors associated with the counting of the smallest cloud droplets by the forward scattering spectrometer probe, the model predictions are very satisfactory—the predictions and the observations are broadly comparable. The underprediction in the sulphate mode can be partly attributed to the fact that observations (S. Osborne 2001, personal communication) showed that some of the fine mode sea-salt particles were internally mixed with some sulphate material, which was not accounted for by the model. However, for the relatively clean stratocumulus-like conditions, it is unlikely that the $N_d$ values (the only variable directly used by climate models) can change because the sea-salt aerosol number concentrations are significantly smaller than the sulphate aerosol concentration. It is important to note that the SO$_4$/NH$_4$ ratio is approximately 0.5—this indicates an encouraging model performance. In table 1, we have also shown the observed and modelled values of the droplet number concentration $N_d$. The figure quoted corresponds to an average of all droplets with a diameter of $2 < D < 19 \mu$m (aerosol particles with diameters less than 2 $\mu$m are not counted as ‘cloud droplets’ and the number concentrations corresponding to diameters greater than 19 $\mu$m are negligible). In table 1, we have used $N_d$ values at 90 m above cloud base but well below the cloud top at 350 m, where cloud top entrainment effects are minimal, yet much of the initial submicrometre aerosol particles have diameters exceeding

Phil. Trans. R. Soc. A (2007)
Considering the fact that there are large error bars in the observations, the modelled $N_d$ values agree favourably with the observations. In addition, some optical properties including the maximum and minimum effective diameters, $D_{\text{eff}}$, and the optical thickness, $\tau$, were also compared with the C-130 observations (Osborne et al. 2000; S. Osborne 2001, personal communication). A general way of estimating the cloud optical depth $\tau$ is given by

$$\tau = \frac{3}{2} \int \frac{q_l(z)}{\rho_w r_e(z)} \, dz,$$

where $\rho_w$ and $q_l$ are the liquid water density and the liquid water content (LWC), respectively, and the integration extends from the cloud base to the cloud top. The above equation for solar visible wavelengths is strictly valid only for a non-absorbing medium where thedrop size is much bigger than the wavelength. $r_e$ is the droplet effective radius, which is the ratio of the third to the second moment of the size spectrum. The optical properties tabulated in table 1 provide an extremely encouraging comparison. The marginal overprediction of $\tau$ is due to the overprediction in the LWC—this is to be expected in the non-entraining parcel model. Entrainment of dry air has a tendency to lower LWC, which is not treated by the model. A detailed study of the chemical processing and optical properties of the ACE-2 stratocumulus for moderately polluted conditions and with the effects of cumulus penetrations has recently been published by Ghosh et al. (2005b). From this latter study, we observe that model results compare extremely favourably with the observations.

By modelling the ACE-2 case study (involving two aerosol types), we demonstrate that the microphysical model is robust, and is amenable to further improvement to include multiple aerosols as well as the effects of internal mixing. Thus, this altered model provides a valuable tool for further studies to relate cloud droplet number concentrations to aerosol masses. These aspects are detailed in the subsequent sections.

### 4. Tricomponent model simulations: biomass smoke activation along with sulphate and sea-salt aerosol

For biomass smoke particles to activate into cloud droplets, it is essential that these particles have some water-soluble components (hereafter designated by the parameter $\epsilon$). Only a limited amount of observational data are available regarding the extent of soluble material present in biomass smoke particles. Sulphates, sodium chloride and other water-soluble salts and inorganic acids are

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Table 1. Modelled and observed microphysical and radiative properties for the ACE-2 case study.

<table>
<thead>
<tr>
<th>parameter</th>
<th>model</th>
<th>observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>min $D_{\text{eff}}$ ((\mu)m)</td>
<td>9.6</td>
<td>(\sim 8.0)</td>
</tr>
<tr>
<td>max $D_{\text{eff}}$ ((\mu)m)</td>
<td>27.3</td>
<td>22.0</td>
</tr>
<tr>
<td>$N_d$ (N cm(^{-3}))</td>
<td>45.7</td>
<td>53 (\pm 20)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>4.1</td>
<td>1.9 - 3.8</td>
</tr>
</tbody>
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common to the atmospheric aerosols and CCN. The abilities of these species to serve as CCN are relatively well known, whereas our understanding of the ability of biomass smoke particles and other organic species to act as CCN is relatively poor and is a critical area of uncertainty in global scale modelling of cloud droplet nucleation. Aerosols from biomass burning are primarily composed of organics and may act as CCN, but some of their CCN activity may actually be due to co-resident inorganic constituents (Van Dinh et al. 1994; Leaitch et al. 1996; Novakov & Corrigan 1996). Measurements from a forested area suggest that biomass burning releases terpene, pinene and other organic acids and some of the products of terpene oxidation may serve as CCN (Leaitch et al. 1999). Virkkula et al. (1999) found that particles from pinene oxidation absorbed some water at an RH of approximately 84%. Cruz & Pandis (1997) examined the CCN activity of particles of adipic and glutaric acids (products of alkene oxidation) and found reasonable agreement with Kohler theory, whereas Corrigan & Novakov (1999) measured much higher activation diameters than predicted by theory.

The preceding discussions suggest that accounting for all the chemical species in biomass smoke particles in a numerical model may be intractable. However, since we are more concerned with the physico-chemical properties, which significantly affect the activation of these particles into cloud droplets, we assume that inorganic sulphate comprises the major contributor to the amount of soluble material in biomass smoke particles. Among recent observational studies of biomass smoke particles, the study conducted by Yamasoe et al. (2000) provides useful information not only on the chemical composition of these particles, but also estimates the amount of soluble material to be expected within these particles. The Yamasoe et al. study was concerned with aerosol particles sampled directly over freshly emitted biomass burning plumes, very close to the sources (approx. 0.5–2 m away from the fire) to characterize direct emissions. From the Yamasoe et al. study, the amount of soluble sulphate material present was approximately 0.25 and this is appropriate for biomass particles that are slightly aged to include some sulphate material. Elemental composition and water-soluble ionic components are reported by Yamasoe et al. only for the fine aerosol mass fraction. This fraction comprises most of the aerosol emissions and corresponds to the most interesting particles for climate change due to their long atmospheric residence time and optical properties. Further details of the experimental procedures can be obtained from Yamasoe et al. (2000). We also assumed that the soluble mass fraction comprised only sulphates and that this mass fraction was representative of both flaming and smoldering emissions. However, we have performed sensitivity tests to study the $N_d$ dependence on $\epsilon$. We examined the cloud droplet spectrum at 90 m above the cloud base for $\epsilon=0.05$, 0.25 and 0.6, corresponding to relatively fresh, moderately aged and fully aged biomass particles at moderate levels of aerosol mass loadings. We find that with increasing values of $\epsilon$, the spectrum broadens to larger sizes. For $\epsilon=0.05$ and 0.25, we obtain a monomodal spectrum with maximum $N_d$ centred around a droplet diameter of 11 $\mu$m but with a broader spectrum for the latter case. For the fully aged case ($\epsilon=0.6$), a second peak develops around a droplet diameter of 13 $\mu$m in addition to a first peak centred around a diameter of 9 $\mu$m, indicating an even broader droplet spectrum. However, most importantly, the total $N_d$ sums up to a value of approximately 177 cm$^{-3}$ in all the three cases. Since the total $N_d$ does not change with increasing values of $\epsilon$, we can conclude...
that parametrized $N_d$ values generated from multiple model runs can be effectively used in host climate models without any loss of generality. In our subsequent analyses, we shall only discuss results corresponding to $\epsilon=0.25$.

Finally, for the sake of completeness, it is important that we also briefly discuss the probable impacts of soot or black carbon, which can also be present along with biomass particles. Soot carbon particles have a much smaller median radius and are less soluble. The Hadley Centre recommends a median radius of 40 nm, which is approximately a third of the biomass median radius. Both soot and biomass aerosol particles have comparable densities, and therefore with comparable mass loadings, sensitivity studies show that biomass particles have a greater influence on the overall $N_d$ values when present with sulphate and sea-salt aerosol. However, in situations where soot carbon mass overwhelms biomass aerosol mass, the $N_d$ values are perturbed by soot aerosol. Work is in progress to develop parametrizations with many possible combinations of sulphate, sea salt, biomass and soot carbon.

Many more sensitivity tests are, of course, necessary to elucidate all the mechanistic details pertaining to fresh and aged smoke in both flaming and smoldering conditions, as well as the presence of other soluble organic constituents in the air masses. Thus, these results should be regarded as a current best approximation, with the estimated sulphate fraction being a reasonable proxy for other hygroscopic components.

(a) Model configuration

Before configuring the model to include biomass smoke along with sulphate and sea-salt aerosol, it is necessary to examine, in particular, how the soluble fraction of the biomass smoke affected the activation of cloud droplets when internally mixed with ammonium sulphate.

In this study, we have not looked at surface tension effects because we have assumed that the solution is still very dilute, so that the surface tension is similar to that for water droplets. Furthermore, electrolyte concentrations in recently activated CCN typically are not large enough to induce a significant change in surface tension (Pruppacher & Klett 1997). However, although a smoke particle may be treated as partially inert (e.g. a pure externally mixed smoke particle), it can contribute to a particle’s size that affects the Kelvin term in the Kohler equation. Similarly, we have not altered the value of the mass accommodation coefficient since, for dilute solutions, it is expected that the value should be close to unity (Wagner 1982).

Some model configuration was necessary to study the effect of the biomass solubility on the droplet activation. The solubility term appears in the expression for the hygroscopicity in the Kohler theory as

$$B = \frac{\nu \phi_s \epsilon M_w \rho_w}{M_{ap} \rho_w},$$

where $\nu$ is the number of ions the salt dissociates into within water; $\phi_s$ is the osmotic coefficient (approx. 1); $\epsilon$ is the mass fraction of the soluble material; $M_w$ is the molecular weight of water; $M_{ap}$ is the molecular weight of aerosol particle; and $\rho_w$ is the density of water.
Clearly, when the fraction of the soluble material in the aerosol particle changes, a corresponding change in the density of the aerosol particles results, which has to be appropriately apportioned. This is done by calculating \( \rho_t \), the effective density with soluble and insoluble material, and can be expressed as

\[
\rho_t = \frac{\rho_s \times \rho_{\text{insol}}}{(\rho_s - \epsilon (\rho_s - \rho_{\text{insol}}))},
\]

where \( \rho_s \) is the density of soluble material (ammonium sulphate 1769 kg m\(^{-3}\)) and \( \rho_{\text{insol}} \) is the density of insoluble material (smoke 1350 kg m\(^{-3}\)).

It is important to note that \( B \) depends on aerosol composition, which determines the number of ions, \( \nu \), the mass fraction of the water-soluble substance, \( \epsilon \), the particle material density and the molecular weight. Thus, from the above equations, we find that \( B \) increases when \( \epsilon \) increases or \( \nu \) increases, assuming that the osmotic coefficient remains unchanged.

The amount of water vapour available during the growth process is strongly dependent on various dynamical aspects and the particle size distribution. Particles carrying more hygroscopic materials consume more water vapour during their growth before reaching the maximum saturation. The maximum saturation ratio reached is typically smaller in the case when we have more soluble material in the nascent droplets than in the case when we have less soluble material in the droplets.

\[ (b) \text{ Microphysical model input parameters} \]

The chemical parcel model was configured with lognormal input aerosol spectra from data currently in use by the UK Met Office (UKMO). Sea-salt observations (O’Dowd et al. 1999c) reveal that the distribution is spread over a fine film mode along with a coarser jet mode. We have allowed the dry aerosol input spectra to correspond to three components with four modes—pure ammonium sulphate, fresh biomass smoke, sea salt (film mode) and sea salt (jet mode). The chosen aerosol mass ranges include low to moderate mass loadings of sulphate and smoke, which, respectively, correspond to clean and moderately polluted urban conditions. Thus, the activation scenario becomes a multidimensional problem with the mass components of the individual species and the resultant \( N_d \) forming the components of a multi-dimensional space. Our results (see §5) clearly indicate that a linear increase in one component mass in one direction does not necessarily evoke a linear response in \( N_d \).

The spectral properties of ammonium sulphate, biomass smoke and sea salt are shown in table 2.

The concentration of sea-salt particles is highly wind speed dependent and is parametrized by the method outlined by O’Dowd et al. (1999c), which is described by the following equations:

\[
\log_{10} N_{\text{film}} = 0.095 U_h + 6.283 \tag{4.2}
\]

and

\[
\log_{10} N_{\text{jet}} = 0.0422 U_h + 5.7122, \tag{4.3}
\]

where \( N_{\text{film}} \) and \( N_{\text{jet}} \) are the sea-salt particle concentrations in the film and jet modes, respectively, expressed in units of particles m\(^{-3}\) and \( U_h \) is the horizontal wind speed in m s\(^{-1}\). The above equations are valid for \( 2 < U_h < 17.5 \) m s\(^{-1}\), and this range covers the range of wind speed values observed by the UKMO (O’Dowd et al. 1999c).
Table 3 lists the trace gas concentrations and the dynamical inputs, both based on the C-130 measurements from the ACE-2 campaign. In addition to the ACE-2 dataset, we also examined the distributions of vertical velocity near the cloud base of a marine stratocumulus that developed off the coast of California (D. Roberts 2002, personal communication). Based on these two datasets, it was inferred that a choice of the most probable updraught velocity of approximately 0.2 m s$^{-1}$ is appropriate for our runs. However, we have undertaken sensitivity studies, where we estimated $N_d$ as a function of varying updraught speeds. We found that at low updraught speeds, when $U < 0.2$ m s$^{-1}$, the $N_d$ values increased rapidly with increasing $U$: $N_d \sim 70$ cm$^{-3}$ at $U \sim 0.1$ m s$^{-1}$, and increased rapidly to 120 cm$^{-3}$ when $U \sim 0.15$ m s$^{-1}$. However, for $0.2 < U < 0.5$ m s$^{-1}$, $N_d$ values ranged between 175 and 200 cm$^{-3}$, indicating a much slower rate of increase. For higher updraught speeds, when $0.5 < U < 2.0$ ms$^{-1}$, the $N_d$ values hardly changed from a value of 200 cm$^{-3}$, indicating that higher values of $U$ can only increase $N_d$ by approximately 10%.

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5. Aerosol activation in a tricomponent domain comprising sulphate, sea salt and biomass smoke

Although the cloud droplet number concentration $N_d$ is a function of three components, the variation of $N_d$ is presented as a function of two components with the third set at specific values. This approach not only facilitates visualization, but also gives a deeper insight into the aerosol activation process.

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In figure 1a, b, we have shown contours of $N_d$ as a function of sulphate and smoke mass loadings at two different salt mass loadings, i.e. 10.287 and 27.646 $\mu$g m$^{-3}$. We observe that the overall number concentrations are largely controlled by the non-sea-salt aerosol. $N_d$ increases linearly with increasing sulphate and smoke masses only for modest values of sulphate and smoke mass loadings. A strong nonlinearity is observed beyond a smoke aerosol mass threshold of approximately 1.5 $\mu$g m$^{-3}$ in figure 1a, b. This is due to the increase in competition for the available water vapour in the air parcel—when there is a preponderance of aerosol particles competing for a limited amount of water vapour, the supersaturation decreases and some of the aerosol particles are not able to grow into cloud droplets, resulting in a fall in $N_d$ values. The effect of increased levels of salt masses is illustrated by comparing figure 1c, d. Introduction of higher levels of salt can also result in a decrease in $N_d$ values, particularly at modest sulphate and high smoke mass levels.

In figure 1c, d, we have shown the $N_d$ variations as a function of smoke and salt masses for modest (figure 1c) and high levels (figure 1d) of smoke mass. In figure 1c, we note that at all levels of sulphate masses, the contour lines are slightly inclined to the left. This clearly indicates that at this level of smoke mass loading, and for all levels of sulphate masses, $N_d$ increases linearly with increasing salt mass loading.

Figure 1. Variation of $N_d$ (N cm$^{-3}$; the marked contour lines) with biomass smoke and sulphate mass for salt mass fixed at (a) 10.287 $\mu$g m$^{-3}$ ($U_h = 5$ m s$^{-1}$; note the nonlinear distribution at high values of smoke mass) and (b) 27.646 $\mu$g m$^{-3}$ ($U_h = 15$ m s$^{-1}$; note that the higher salt mass has a perturbing effect on the distribution at low sulphate and high smoke levels). Variation of $N_d$ (N cm$^{-3}$; the marked contour lines) with sulphate and salt masses for smoke mass fixed at (c) 1.1506 $\mu$g m$^{-3}$ (note the linear contour lines) and (d) 2.3013 $\mu$g m$^{-3}$ (note that the higher smoke loading induces a nonlinear $N_d$ variability).
With the introduction of further amounts of smoke (figure 1d), the linear and predictable picture of the $N_d$ variability completely disappears—at high levels of salt (in excess of 20 $\mu$g m$^{-3}$), $N_d$ values start to fall appreciably.

The complex and often nonlinear dependence of $N_d$ on aerosol mass loadings is best illustrated by examining specific slices through the multicomponent domains. We show one such slice in figure 2. The overall higher number concentrations in figure 2 are due to the high sulphate loading. For similar amounts of aerosol masses of the three species, our simulations indicate that sulphate aerosol particles are the most effective for elevating values of $N_d$. Sulphate aerosol particles yield three ions in an aqueous solution, are highly soluble and as a result can have a significant impact on the solubility term in the Kohler equation. In figure 2, we clearly observe that $N_d$ first increases linearly with increasing smoke loadings and beyond a smoke threshold of approximately 1.5 $\mu$g m$^{-3}$, the $N_d$ values are almost halved with further increases in the smoke mass levels.

In the preceding paragraphs we have amply demonstrated that in a multicomponent domain, the activation of cloud droplets from aerosol particles is a complicated process. Although, intuitively, one would expect that $N_d$ should increase with increasing aerosol loadings, we have seen that this is not always true. Since global climate models worldwide use $N_d$–aerosol number concentration relationships in a closed parametric form for both microphysical and radiative transfer calculations, any misrepresentation of $N_d$ values is likely to induce some further uncertainties in climate predictions. It is therefore appropriate at this stage to briefly discuss some current methods employed to estimate $N_d$ from aerosol number concentrations. The Hadley Centre currently uses a modified version of Jones et al. (2001) relationship, which takes sulphate, sea-salt and biomass-burning aerosols as input. Sea-salt number concentrations are obtained directly from a sea-salt parametrization (O’Dowd et al. 1999b); sulphate and biomass are converted from mass concentration to number concentration, assuming lognormal size distributions. All the number concentrations are then just simply added to give the input number concentration. Thus, an external mixture is always assumed. In effect, the combined

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relationship reduces to

\[ N_d = 375(1 - \exp[-0.0025A]), \] (5.1)

where \( N_d \) is expressed in \( \text{N cm}^{-3} \), \( A = A_{\text{SO}_4} + A_{\text{SS}} + A_{\text{biomass}} \), and the \( A \)s are the number concentrations of sulphate, sea-salt film, jet modes and biomass aerosol, respectively.

In the formulation described in equation (5.1), one assumes that \( N_d \) approaches a maximum value of 375 \( \text{cm}^{-3} \) asymptotically. In addition, a smooth asymptotic increase is always achieved. We have compared our \( N_d \) predictions with values obtained from (5.1) under similar conditions and find that equation (5.1) underpredicts the overall \( N_d \) values. The underprediction is more pervasive (up to 50 \( \text{cm}^{-3} \)), particularly at high aerosol mass loadings. In addition, the oversimplified predictions from equation (5.1) also fail to capture the nonlinear dependence of \( N_d \) on aerosol mass loadings. We have just described (figure 1a, b) that the \( N_d \) variation can be often nonlinear and complex in a multicomponent domain beyond certain critical aerosol mass loadings for specific components. In addition, equation (5.1) assumes pure external mixtures. In reality, aerosol particles, particularly over polluted urban areas and over air contaminated by forest fire emissions, are often internally mixed with various other component species. Biomass smoke observations (e.g. Yamasoe et al. 2000; Okada et al. 2001) indicate that these particles are generally internally mixed with some sulphate material. In an \( \text{SO}_2 \)-rich polluted urban air mass, the amount of soluble sulphate material that can internally mix with a biomass aerosol particle can be high. In the present study, therefore, we have allowed the biomass particles to be internally mixed.

Before concluding this section, it is appropriate to discuss the implications of including many more species than the three components studied thus far. From our experience so far, we can state that \( N_d \) can vary monotonically with increasing aerosol masses for a two-component system comprising sulphate aerosol and a fixed amount of sea salt. A third component, i.e. biomass aerosol, leads to a complex dependence of \( N_d \) on the aerosol masses. The anomalous dependence of \( N_d \) on aerosol loading when sea-salt particles are introduced into the aerosol mixture becomes much more pronounced when additional components with differing chemical and physical characteristics are incorporated. If we add a fourth component, with similar spectral properties, we anticipate further changes, provided it has enough soluble material. Under these conditions, the fourth component is likely to modulate the environmental saturation ratio on which aerosol activation is crucially dependent. Finally, sensitivity tests show that with the same median radii, when one chooses a narrower s.d. for the lognormal spectrum, much more complex and nonlinear behaviour is obtained in the \( N_d \) variations. Overall, we find that a broader s.d. has a smoothing effect on the \( N_d \) variation.

6. Wider implications and concluding remarks

The most important result from this study is that, when sulphate aerosol, biomass smoke and sea salt simultaneously contribute to the cloud droplet activation process, the resultant cloud droplet number concentration \( N_d \) cannot be estimated straightforwardly, as is done for situations when only sulphate and/or sea-salt aerosol are present. In a tricomponent activation domain, \( N_d \) can
vary in a complicated nonlinear way under certain conditions, and this feature should be recognized by GCMs. This will require the use of sophisticated interpolation schemes (rather than simple parametrized relationships described by equation (5.1)) that can accurately model the $N_d$ variability. Such numerical schemes are essential to fully integrate the cloud droplet number concentration variability in multicomponent aerosol systems (Rap et al. submitted). These schemes should be numerically cost-efficient, should yield an exact fit to the data generated by multiple model runs and should include a realistic progression of interpolated values from one data point to others in its vicinity. We believe that the results presented in figures 1 and 2 will aid climate modellers worldwide to obtain reasonable estimates for $N_d$ since the graphs cover an exhaustive range of input aerosol masses.

Our simulations show the maximum sensitivity to sulphate aerosol. The sulphate particles and some of the film mode salt particles have radii within the accumulation mode of an aerosol spectrum. These aerosols can hydrate to diameters between 0.1 and 2 µm where their mass extinction efficiency is the largest. Accumulation mode aerosols not only have high scattering efficiency, but also have long lifetimes and very efficiently form CCN (IPCC 2001). The effects of biomass smoke are sensitive to values of sulphate and sea-salt loadings.

The complex and nonlinear $N_d$ variations shown in figures 1 and 2 can impact both the first and second indirect effects. The first indirect effect is modelled by allowing the cloud droplet effective radius used in radiation schemes in GCMs to be calculated from $N_d$–aerosol concentration parametrizations. As a result, any discrepancies in $N_d$ estimates are likely to affect estimates of the first indirect effect. We now discuss the possible implications of this variability on the second indirect effect.

The early stages of cloud droplet growth occur by the condensation of water vapour onto CCN when the RH just exceeds 100%. However, the rate of condensational growth slows as the droplets grow to larger sizes, and this process on its own cannot account for the production of precipitation-sized particles in warm clouds over the times observed (Pruppacher & Klett 1997). Precipitation formation in warm clouds is governed by a stochastic process whereby a small fraction of cloud droplets grow rapidly and have appreciable fall speeds relative to other cloud droplets. This triggers the collision–coalescence process. In GCMs, this partitioning of cloud water into rain water is achieved through an ‘autoconversion term’. For the same cloud water content, autoconversion is slower for a high concentration of smaller droplets than for a low concentration of larger droplets. This mechanism therefore has a large bearing on the second indirect or the lifetime effect. Autoconversion parametrizations used in some GCMs use the Tripoli & Cotton (1980) scheme, which calculates an autoconversion rate and a threshold (Jones et al. 2001).

When we calculated the autoconversion rates from Tripoli & Cotton (1980) and used the $N_d$ distribution in figure 1a, we observed a significant amount of variability in the autoconversion rates—the maximum value of $9.96 \times 10^{-7}$ s$^{-1}$ is almost double that of the minimum value of $5.73 \times 10^{-7}$ s$^{-1}$. Furthermore, autoconversion is allowed to proceed once cloud liquid water exceeds a threshold minimum and ideally this threshold $q_{\text{min}}$ should depend on aerosol concentration. The value of $q_{\text{min}}$ ranges from approximately 0.005 g kg$^{-1}$ in remote regions to approximately 1.2 g kg$^{-1}$ close to polluted regions in urban areas, indicating that $N_d$, and therefore
aerosol concentration, has a double impact on autoconversion: high values not only
suppress the rate, but also increase the threshold (Jones et al. 2001).

There is another area of cloud microphysics that is being actively pursued
worldwide and which has a direct bearing on the present study—this pertains to the
quantification of the settling rates of cloud droplets. In current models, the cloud
droplets are prescribed with still air settling speeds. In reality, clouds are turbulent
and when cloud droplets settle past microscale eddies inherently present in
turbulent clouds, recent calculations show that droplets with radii approximately
10 μm do indeed settle faster than their still air fall speeds (Davila & Hunt 2001;
Ghosh et al. 2005a). Rogers & Yau (1989) suggest that autoconversion will only
proceed once the number concentration of cloud droplets greater than 20 μm in
radius exceeds approximately 10^3 m^{-3}. When cloud droplets settle faster in
turbulence, it is expected that the autoconversion process will be more efficient,
since the rate at which cloud droplets with radii in excess of 20 μm form will be
faster. We therefore observe that autoconversion rates can be highly variable not
only due to N_d variability (as in figures 1 and 2) induced by competing aerosol effects
in a multi-aerosol environment, but also due to the changes induced by turbulence-
assisted settling rates of cloud droplets. Both these factors are important and we
hope to carry these ideas forward within the framework of GCMs in the future.

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