Atmospheric sulphur and cloud condensation nuclei in marine air in the Southern Hemisphere

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SUMMARY

Measurements of atmospheric sulphur species made in Southern Ocean air, at the Cape Grim Baseline Air Pollution Station, are reviewed in an attempt to discern the role played by oceanic emissions of dimethyl sulphide (DMS) as a source of cloud condensation nuclei (CCN). Consistent with conclusions reached by others, our data indicate that the connection between DMS concentration and CCN concentration is neither simple nor direct, being mediated through a range of chemical pathways and intermediate species that are subject to considerable variability over timescales ranging from minutes to months. Physical and meteorological processes are no less important than chemical processes as sources of complexity in the DMS → CCN transformation process. Moreover, the considerable uncertainty that currently exists about both the number of chemical pathways involved in DMS oxidation, and the kinetic coefficients associated with the proposed pathways, make quantitative modelling studies problematic.

Nevertheless, synthesis of a large body of data available from Cape Grim and other Southern Ocean sites does permit some refinement of our understanding of the DMS–CCN connection. Here, these data are employed to illustrate the current state of knowledge about the connections between DMS, CCN and cloud properties at Cape Grim, and to highlight the many complexities that underlie these connections.

1. INTRODUCTION

Continuous measurement of atmospheric constituents at the Australian baseline station located at Cape Grim, north-western Tasmania, commenced 20 years ago in April 1976. Among the small suite of initial measurements were aerosol microphysical measurements, in the form of condensation nuclei (CN) measurements, and aerosol ionic composition measurements (i.e. soluble ions) via high volume aerosol sampling for subsequent chemical analysis. By 1980, ongoing cloud concentration nuclei (CCN) measurements had been added, with routine size-segregated aerosol sampling and gaseous dimethyl sulphide (DMS) measurements coming on-line in 1988. Sulphur dioxide (SO₂) measurements were instituted in 1990, while high resolution impactor sampling for determination of aerosol chemical size distribution began in 1993. Also added in the early 1990s were aerosol optical absorbance measurements, and aerosol number size distribution measurements made with both a laser-based aerosol size spectrometer and a differential mobility analyser, supplanting earlier CN size distribution measurements derived from a diffusion battery and CN counter.

Throughout the expansion of this continuous measurement programme a regular sequence of in-

tensive, short-term field studies has been carried out, both at Cape Grim and at other Southern Hemisphere sites, ranging from surface and ship-borne measurements to airborne and satellite-derived measurements, with a focus on specific atmospheric processes rather than on the chemical climatology of aerosol and related species. In recent times these studies have been supported by a range of modelling activities (e.g. Ayers *et al.* 1995a).

The 20 years of aerosol and aerosol-related observations at and around Cape Grim provide a substantial body of information relevant to the hypothesized connection between marine aerosol (DMS-derived sulphate aerosol in particular), CCN, cloud albedo and climate (Charlson *et al.* 1987). The aim here is to extract key elements from the various studies undertaken to date at Cape Grim, and synthesize these into a review and discussion of our current scientific understanding of marine aerosol properties at this site within the context of the DMS–CCN–cloud albedo–climate hypothesis.

2. CN, AEROSOL SIZE DISTRIBUTION AND CCN

CCN form a subset of CN, the latter representing the total aerosol number concentration summed across all sizes. Figure 1 presents the average summer aerosol size distribution at Cape Grim (Gras 1995) in both

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Figure 1. Average Cape Grim summer aerosol number distribution, taken from Gras (1995), presented against both logarithmic and linear ordinates, showing also the CCN size ranges activated at supersaturations of 1.2, 0.75 and 0.23%.

Figure 2. Average seasonal cycles in marine CCN number concentration at Cape Grim (Gras 1989, 1990, 1995).

Figure 3. Cape Grim summer aerosol distribution from figure 1 reproduced on a linear ordinate as both number and volume size distributions.

logarithmic and linear concentration units, with the size ranges corresponding to CCN active at 0.23, 0.75 and 1.2% supersaturation (S) also identified. A significant annual cycle in CCN concentration is observed at Cape Grim (Gras 1990), as shown in figure 2.

(a) Sources of CCN material

The focus here is on the soluble ionic components of the Cape Grim aerosol, since it is these components that are thought to comprise the CCN (Bigg *et al.* 1984; Charlson *et al.* 1987). The early Cape Grim high volume aerosol records indicated, not surprisingly, that two major components make up the soluble aerosol component: sea salt, and non-sea salt (NSS) sulphur species, primarily as sulphate and methanesulphonate (MSA) (Ayers *et al.* 1986). However, the relationship between aerosol volume (or mass) and number concentration is such (see figure 3) that although the micrometre-sized particles dominate the volume and mass distributions, the number distribution of CN and CCN is dominated by the submicrometre (a few tenths of a micrometre), and smaller particles.

Conventional wisdom has it that the micrometre-sized soluble particles in marine air are composed of sea salt, with the tenth micrometre and smaller particles composed of sulphate and MSA. Figure 4, displaying sodium, chloride and non-sea salt sulphate (NSSS) data from a Cape Grim impactor sample collected during the 1993–1994 summer, confirms this (compare the shape of the mass distribution in figure 4 with the volume distribution in figure 3). Thus, the discussion here centres on the sea salt and sulphur components of the aerosol, and the factors that regulate their atmospheric levels and variations with season.

(b) Factors regulating CCN numbers and size distribution

(i) Precursor gas (DMS) concentration

The source of submicrometre aerosol sulphur over remote oceans is caused by DMS emission from biological processes in the oceanic surface waters. Measurements of atmospheric DMS at Cape Grim presented by Ayers *et al.* (1995a) show a pronounced annual cycle (see figure 5) with a maximum in summer and minimum (approaching zero) in winter that is consistent with the expected summer maximum/winter minimum in marine biological productivity. Therefore, the seasonal cycle of atmospheric DMS mirrors the oceanic source function, as confirmed recently by a numerical model study of the surface water biological

Figure 4. Measured Cape Grim aerosol mass distributions (MOUDI impactor, summer 1993–1994).

Figure 5. DMS seasonal cycle at Cape Grim, showing individual 1 h data recorded between November 1988 and December 1993. The line depicts the monthly mean values (Ayers *et al.* 1995a).

Figure 6. Time series of monthly mean CN and aerosol MSA concentrations at Cape Grim (Ayers *et al.* 1986; Gras 1989).

processes in the Southern Ocean (Gabric *et al.* 1995). Since atmospheric oxidation of DMS provides the aerosol NSSS and MSA that dominate the sub-micrometre aerosol component (figure 4), and since this component dominates the CN and CCN number concentrations (figure 3), it is clear that the seasonal cycles in CN and CCN concentration (figure 2) derive largely from the seasonality in the oceanic DMS source. This is particularly well illustrated by the multi-year CN (Gras 1989) and MSA time series presented in figure 6.

(ii) Wind speed

While DMS production in ocean surface waters provides the driving force for air–sea transfer of DMS, and thus seasonality in this important atmospheric sulphur source function, the efficiency of air–sea transfer also asserts significant control on the resultant atmospheric DMS concentration. The DMS air concentration is important because the actual flux of sulphur from DMS into CN/CCN precursors and aerosol end products, via gas phase oxidation processes,

Figure 7. Mean wind speed dependence of atmospheric DMS concentration determined from more than 800 half-hourly DMS measurements made at Cape Grim in early December 1993 by Ayers *et al.* (1995b). The line depicts the relationship expected on the basis of the Liss & Merlivat (1986) specification for air–sea transfer as a function of wind speed.

depends directly (as a first order chemical process) on the DMS concentration.

The major determinant of air–sea transfer efficiency is wind speed, with the transfer function thought to be a strong and nonlinear function of wind speed (Liss & Merlivat 1986). This expectation was borne out by an analysis of the wind speed dependence of atmospheric DMS concentration during the 1993–1994 summer at Cape Grim (Ayers *et al.* 1995b), reproduced in figure 7.

Wind speed is not only important as a regulator of DMS concentration, and thus the availability of oxidizable sulphur. It has also been shown empirically to be the major determinant, again in a strongly nonlinear way, of the concentration of sea salt particles in the marine boundary layer. Bigg *et al.* (1995) conveniently summarize the pioneering works of Woodcock & Blanchard, and go further by providing empirical evidence from work at latitude 50°–54° S over the Southern Ocean of a wind speed dependence not only for sea salt particles, but also for CN and CCN. As shown in figures 3 and 4, the CN and CCN must include particles containing sulphate below the sea salt size range. The overall average CCN wind speed dependence determined by Bigg *et al.* (1995) for CCN is depicted in figure 8.

Since CCN extend down in size below the range, having a significant sea salt component, only part of the observed dependence can be due to wind stress-induced sea salt production. Other non-sea salt particles must also be involved. This accords with the non-zero intercept of 30–40 cm⁻³ active at 0.23% evident for the empirical CCN vs MSA and CCN vs DMS relationships at Cape Grim at zero MSA or DMS (Ayers & Gras 1991; Ayers *et al.* 1995a). This intercept is too large to be explained entirely by sea salt, implying an additional non-DMS, non-sea salt source of CCN, which, given the fact that aerosol NSSS concentration does not approach zero as MSA and DMS approach zero in winter (Ayers *et al.* 1991), further suggests that the additional source involves CCN composed of sulphate.

Figure 8. Average wind speed dependence of CCN concentration (0.1–0.6% supersaturation) determined by Bigg *et al.* (1995) for the Southern Ocean at latitude 50°–54° S.

Raes (1995) suggests that entrainment from above the boundary layer may be an important source of CN and CCN that continuously ‘seeds’ the marine boundary layer with sulphate particles from aloft. Entrainment has been shown to be involved in maintenance of marine boundary layer ozone levels (Ayers *et al.* 1996a), and has also been invoked in recent explanations of observed patterns in sulphur gas and aerosol species measured in equatorial marine air at Christmas Island (Clarke *et al.* 1996). Entrainment can be anticipated to increase with the increasing levels of turbulent kinetic energy in the lower atmosphere that accompany increases in wind speed, providing an increase in the rate of boundary layer ‘seeding’ by sulphate particles, if the hypothesis of Raes is correct. Thus, entrainment may provide an explanation (at least in part) for both the wind speed dependence of CN and CCN concentrations over the Southern Ocean and the relatively high wintertime sulphate levels observed at Cape Grim.

Finally, although we do no more than note the issue here, any change in wind speed induced by a change in climate could also have a significant effect upon DMS production in the ocean surface, since mixed layer depth is important to nutrient availability, which underpins the biological DMS production processes (Gabric *et al.* 1993), and mixed layer depth is a function of wind stress.

(iii) Cloud processes

The number–size distribution in figure 1 shows clearly a trimodal shape that is now known to be a characteristic of marine air (Hoppel *et al.* 1990; Hoppel & Frick 1990; Fitzgerald 1991). The upper size mode is readily attributed to sea salt. Hoppel *et al.* (1990) proposed that the characteristic bifurcation at 0.02–0.03 μm radius between the two modes at 0.01 and 0.1 μm was the result of regular cloud processing of boundary layer air (i.e. repeated condensation–evaporation cycles) in non-precipitating clouds. CCN larger than the critical size in a given cloud element would be activated, the resultant droplets would efficiently scavenge soluble gases such as SO_2 (which

Figure 9. Modelled effect on aerosol size distribution of a single condensation evaporation cycle in a summertime cloud at Cape Grim. The model used was that of Ayers & Larson (1990), initialized at 99% relative humidity and 900 hPa. Assumed gas concentrations were 25 pmol mol^{-1} each for SO_2 and NH_3 , 1.5 nmol mol^{-1} for H_2O_2 , and 15 nmol mol^{-1} for O_3 .

would be oxidized rapidly to aqueous sulphate) and add dissolved mass to the droplet, which upon droplet evaporation would then return to the atmosphere a particle larger in radius than the initial CCN.

Figure 9 contains a model simulation of a single cloud condensation–evaporation cycle, employing an adiabatic cloud model (Ayers & Larson 1990) having size-resolved droplet chemistry and explicit representation of the separate sulphate and sea salt CCN. The model was initialized with a bimodal representation of the Cape Grim summer aerosol size distribution and chemical boundary conditions appropriate for Cape Grim in summer (25 pmol mol^{-1} SO_2 and NH_3 , 1.5 nmol mol^{-1} H_2O_2 (hydrogen peroxide), and 15 nmol mol^{-1} O_3 (ozone)). The simulation reproduces the major features of the observed trimodal size distribution after only a single cloud passes, readily confirming Hoppel’s suggestion that clouds themselves exert a powerful influence on CN and CCN size distribution properties.

(iv) Microphysical/chemical interactions

Detailed measurements of CCN chemical properties suggest a range of subtle interactions across the size range that play a role in determining aerosol composition as a function of size. Three illustrations are given here. First, consider the acid–base properties of the aerosol and the effect of this balance on aerosol composition. Figure 10 shows an example of relevant data derived from MOUDI (Micro-Orifice Uniform Deposit Impactor) collections in summertime at Cape Grim. The data consist of an ion imbalance parameter, IB, and the mole ratio of chloride to sodium, both plotted as a function of particle size. The IB values go negative at submicrometre particle sizes in concert with a strong decrease in chloride to sodium ratio. Both features have their explanation in the fact that they occur at the size where NSSS content is maximal (figure 11). This leads to a strongly acidic aerosol at around 0.1 μm in radius, which causes an apparent lack of cations in the IB parameter since free acidity

Figure 10. Chloride to sodium ratio and ion imbalance (cation sum minus anion sum divided by their mean, expressed as a percentage) as a function of size from a Cape Grim summertime MOUDI impactor sample.

Figure 11. NSSS distribution from a Cape Grim summertime MOUDI impactor sample, determined in the usual way assuming sodium acts as a conservative tracer for sea salt sulphate. The region plotted with a broken line is that where uncertainty in the sea salt subtraction from total sulphate becomes large.

Figure 12. MSA and associated aerosol surface area distributions from a summertime Cape Grim MOUDI impactor sample. The surface area distribution was derived by summing the masses of all ionic components at each size and determining a volume distribution assuming a uniform particle density (2 g cm^{-3}).

(H^+ ion) is not determined in the chemical analyses. It leads concurrently to a deficit in sea salt chloride at the same particle sizes, due to volatilization of HCl.

Figure 13. As for figure 12, except oxalate instead of MSA.

A second aerosol property thought to be important in determining the fate of condensing gaseous species is aerosol surface area, with gas deposition predicted to go as a function of size with aerosol surface area. Figure 12 shows the aerosol surface area distribution computed from the total mass distribution, assuming a mean particle density of 2 g cm^{-3} , plotted with the aerosol MSA distribution. Comparison with figure 4 shows the expected decrease in mode radius for surface area, compared with mass (represented by sodium and chloride in figure 4). The surface area–MSA comparison in figure 12 clearly shows that the upper MSA mode corresponds extremely well with the surface area mode, providing support for the hypothesis that the upper mode results from gas–aerosol condensation.

This conclusion is reinforced by figure 13, where the condensing species is oxalic acid rather than MSA, with the oxalic acid likewise showing a mass mode coincident with the surface area mode. The effect of strong acidity due to NSSS at about $0.1 \mu\text{m}$ is again evident in this case, since oxalic acid, though a strong acid, is much less strong and more volatile than both sulphuric and methanesulphonic acids, so in analogy with the loss of HCl, oxalic acid fails to deposit effectively at the size of the NSSS/MSA fine particle mode.

Finally, just as the weaker acids are unable to condense on particles composed of stronger (i.e. sulphuric and methanesulphonic) acids, the data indicate that gaseous ammonia is not taken up at micrometre and larger sizes despite some deposition of MSA and NSSS by condensation on particles at these sizes. The reason is that micrometre-sized particles are primarily composed of sea salt, which is sufficiently alkaline to prohibit the uptake and ionization of the weakly alkaline ammonia gas. This is clearly evident from figure 14, which presents both the ammonia size distribution and ammonia/NSSS ratio from a summertime Cape Grim MOUDI sample.

(v) DMS oxidation

Clearly underlying the foregoing discussion is the recognition that the major source of CCN number at Cape Grim is DMS, from which the most numerous small particles consisting of acid sulphate (SO_4^{2-})/MSA are derived. Thus, there is a need to understand the

Figure 14. Ammonium and $\text{NH}_4^+/\text{NSSS}$ mole ratio distributions from a summertime Cape Grim MOUDI impactor sample.

$\text{DMS} \rightarrow \text{SO}_4^{2-}/\text{MSA}$ conversion process as a central component in the hypothesized DMS–CCN–cloud albedo–climate feedback. However, DMS oxidation is complex, and at this stage not well understood, as is evident from the two conference volumes and the most recent journal publications that give attention to this issue (e.g. Plane 1989; Turnipseed & Ravishankara 1993; Saltelli & Hjorth 1995).

The availability at Cape Grim of lengthy data records for DMS, SO_2 , aerosol NSSS and MSA has provided an opportunity to test some aspects of current ideas about DMS oxidation. Two questions in particular have provided an initial focus. Are the levels of SO_2 , NSSS and MSA consistent with the available DMS supply, or are other sources of sulphur required to describe the boundary layer sulphur budget at Cape Grim? Is temperature an important variable in determining the relative proportions of MSA and NSSS resulting from DMS oxidation?

The first question arises from the observation mentioned above that CCN levels at Cape Grim show a significant intercept (30–40 cm^{-3} at 0.23% supersaturation) when monthly mean CCN level is plotted against monthly mean DMS level (figure 15). The second question arises because the effect of temperature on the initial DMS oxidation path by OH (i.e. abstraction vs addition pathways) has been taken to explain the observed increase in MSA/NSSS with increasing latitude/decreasing temperature (Bates *et al.* 1992), whereas at Cape Grim this ratio is observed to decrease with temperature when the ratio is plotted as a function of season (figure 16).

These questions have been addressed using a boundary layer box model of DMS oxidation, based on the very comprehensive oxidation scheme of Yin *et al.* (1990), with temperature dependencies added to two of the central reaction paths, the unimolecular decomposition pathways of the radicals CH_3SO_2 and CH_3SO_3 . Temperature dependencies were determined empirically, as described in detail by Ayers *et al.* (1996b), based on comparisons between observed and modelled atmospheric levels of DMS, SO_2 , MSA and NSSS at equatorial and mid-latitude sites, constrained by the estimated activation energies discussed by Turnipseed & Ravishankara (1994). Other details of

Figure 15. Bivariate plot of long-term monthly mean CCN and DMS data from Cape Grim (Ayers *et al.* 1995a). Both sets of data have been normalized by dividing the individual monthly values by the dataset mean. The CCN intercept at zero DMS lies in the range 30–40 cm^{-3} .

Figure 16. Time series of MSA/NSSS mole ratio at Cape Grim, from weekly high-volume aerosol samples collected with an upper particle size cut-off of 5 μm aerodynamic diameter.

the model parameterizations and boundary conditions employed are discussed by Ayers *et al.* (1995a) and Ayers *et al.* (1996b).

Table 1 contains comparisons between mean January (summer) and July (winter) observations and model predictions at Cape Grim, as presented by Ayers *et al.* (1996b). In both cases, the model DMS surface fluxes were chosen to reproduce the observed Cape Grim atmospheric DMS levels, this being necessary to provide an initial constraint in terms of DMS available for oxidation. The results (table 1) suggest that the summertime balance between DMS oxidation and the measured product species levels is reproduced adequately by the model, as is the MSA/NSSS ratio. For the situation in winter, the MSA level produced by the model is consistent with the DMS levels, but modelled NSSS is a factor of two lower than the observed amounts, while modelled SO_2 is a factor of four lower than the observed amounts. Despite this mismatch, which again suggests that another source of non-DMS-derived sulphur exists in winter at Cape Grim, the modelled wintertime MSA/NSSS ratio is

Table 1. *Observed and modelled sulphur species atmospheric mole fractions at Cape Grim, pmole mole⁻¹ (Ayers et al. 1996b)*

	observed	modelled
January		
DMS	120	120
DMS	17	17
NSSS	76	76
SO ₂	8	6
MSA/NSSS	0.23	0.23
July		
DMS	15.3	15.3
MSA	0.7	0.6
NSSS	~ 8	4
SO ₂	~ 1.9	0.5
MSA/NSSS	~ 0.09	0.16

lower than the summertime value, which is consistent in trend with the Cape Grim observations and contrary to the simple argument based on OH–DMS abstraction/addition rates (Bates *et al.* 1992). The fact that the observed SO₂ and NSSS levels in winter are so much higher than those that can be derived from the model when it is constrained by the observed atmospheric DMS level strongly reinforces the argument made earlier, based on non-zero CCN levels in winter, that another source of sulphate CCN exists at this time of year. Other important conclusions that may be reached given the generally good performance of the model (see table 1) are that temperature dependencies other than those involved in the initial OH attack on DMS are important for adequate simulation of the available observations.

The amount of additional NSSS and SO₂ that would be required from non-DMS sources to bring the modelled and observed wintertime data in table 1 into agreement is small, given the strong wintertime depression in levels of all species. At this stage no measurements are available from Cape Grim to identify possible additional sources, however, it is worth noting that given the small quantity required these might include not only other reduced sulphur gases, but also long-range transport from the Australian continent or other more distant continental sources, and entrainment of sulphate from the lower free troposphere.

(vi) CCN–cloud–climate interactions

Monthly mean data from the Cape Grim time series have been used (Ayers & Gras 1991; Boers *et al.* 1994; Ayers *et al.* 1995a) to show empirical relationships between DMS, CCN and satellite-derived cloud albedo that are consistent with the hypothesized relationship between cloud optical properties and DMS emissions (Charlson *et al.* 1987). Figures 15 and 17 reproduce some of these data to reveal the clear structural relationships that may be found. Boers *et al.* (1994) simulated the seasonal variation in cloud optical depth using the observed seasonal cycle in CCN to force an adiabatic cloud model, and concluded that the seasonal

Figure 17. Bivariate plot of long-term monthly mean satellite-derived cloud optical depth and CCN concentration data from Boers *et al.* (1994). Both sets of data have been normalized by dividing the individual monthly values by the dataset mean.

variation in satellite-derived optical depth was largely explicable by the CCN variations, though other factors (not modelled) were probably influential as well.

Subsequently, Schwartz & Slingo (1996) estimated cloud top albedo from the cloud optical depth data of Boers *et al.* (1994), and concluded that the sensitivity of estimated cloud top albedo to variation in CCN concentration was a factor of 3.5 lower than expected, suggesting a need to include additional factors in the analysis. Boers (1995) did extend the modelling work of Boers *et al.* (1994), considering not only the effects of CCN but also two important additional factors that control cloud depth, solar radiation and drizzle. Profound effects on the seasonal variation of cloud optical depth resulted when each of these factors was added to the model, leading to the conclusion that ‘seasonal variability in cloud optical depth directly due to variations in CCN–DMS concentration can be easily masked if the two compensating mechanisms are slightly out of phase, or if one dominates the other’. This led to additional conclusions that ‘... great care needs to be taken in estimating the effect of CCN on cloud albedo ... the dynamic adjustment of cloud depth to changing external conditions is an important element which up to now has received little attention’ (Boers 1995). Thus it is not only the biological processes that regulate DMS emission, and the atmospheric chemical processes that regulate aerosol formation from DMS that contain complexities sufficient to render quantitative modelling difficult at the current state of understanding: the same is true for the nexus between CCN and cloud optical properties, even at a site like Cape Grim where upwind conditions are probably as homogeneous as it is possible to find anywhere on the planet.

3. CONCLUDING REMARKS

We have reviewed briefly information on atmospheric sulphur species, cloud condensation nuclei and cloud properties produced during 20 years of

measurements made in Southern Ocean air at or near the Australian baseline station located at Cape Grim, Tasmania. Compelling empirical evidence has evolved from these measurements showing clear seasonal relationships between atmospheric dimethyl sulphide, three of its atmospheric oxidation products (sulphur dioxide, methanesulphonate and non-sea salt sulphate), levels of condensation nuclei and cloud condensation nuclei, and cloud optical depth. Relationships such as these may be viewed as necessary (though not sufficient) conditions underpinning the hypothesis of a climate regulation role for oceanic phytoplankton (Charlson *et al.* 1987). In that sense, these observations provide significant support for this hypothesis.

However, at the more detailed level necessary for development of a unified, quantitative understanding of the proposed climate feedback loop, many complexities become evident, making straightforward interpretation and modelling difficult at present. From analysis of the Cape Grim data it is possible to identify a variety of confounding factors that require consideration in any attempt to model the response of the DMS–CCN–cloud albedo system to any hypothesized change in climate.

One example is wind speed, which could well be affected in a secular way by a change in climate, and has multiple potential influences on the marine atmospheric sulphur cycle. For example, change in wind speed will affect the oceanic mixed layer depth, which influences nutrient availability in the ocean surface and DMS production: it affects DMS air–sea transfer efficiency, sea salt CCN production, and apparently it affects other factors such as boundary layer-free troposphere entrainment rate that influence directly the total CCN concentration.

Another example concerns the marine stratiform clouds that are the climate-forcing agents in the Charlson *et al.* (1987) hypothesis: yet change in climate may well lead to concomitant change in CCN size distributions and cloud dynamics via changes in cloud processing and drizzle rate, respectively, that have nothing to do with DMS.

Final examples are the widely discussed complexities of DMS oxidation (Saltelli & Hjorth 1995) and aerosol formation processes (Pandis *et al.* 1995; Raes & Van Dingenen 1995), which have not been discussed in detail here but must be acknowledged as being far from quantitatively understood.

Clearly a great deal is now known about DMS, the marine atmospheric sulphur cycle, CN and CCN at Cape Grim. However, considerable additional understanding of many marine environmental processes remains to be achieved before a quantitative prediction of the hypothesized climate regulation capabilities of marine phytoplankton can be made.

This work rests in large part on the careful, skilful and dedicated efforts of many Cape Grim staff over many years, without whose enthusiastic assistance the measurement programme could not have been undertaken. The Cape Grim programme is funded by the Commonwealth of Australia, and is administered jointly by the Bureau of Meteorology and CSIRO.

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- G. P. AYERS. I agree entirely that the cloud base dynamics determine which subset of CN act as CCN in a given situation. However, we do know that the ability of particles to act as CCN is a function of size, largest particles being activated first with particles of decreasing size activating as the peak supersaturation near cloud base increases. So I think it is reasonable to say that all soluble particles down to a certain size can be expected to act as CCN, and it is only that lower limit that varies with updraft velocity/supersaturation. And that lower size as a function of supersaturation is reasonably well known for common types of CCN (e.g. sea salt or ammonium sulphate particles).
- M. H. SMITH. Is there any seasonal variability in cloud droplet concentrations or mean radius to correlate with the changes in CCN concentrations?
- G. P. AYERS. Yes. At Cape Grim the seasonal variance in CCN concentration does decrease as supersaturation decreases, which is exactly what would be expected on the basis of my previous answer, since the seasonal variation in the CN number distribution becomes less at larger sizes, that is, at lower supersaturations (see Gras, J. L. 1995 CN, CCN and particle size in Southern Ocean air at Cape Grim, *J. Atmos. Res.* **35**, 233–251).
- There is evidence of the expected seasonal variability in cloud droplet concentrations upwind of Cape Grim, based on a seasonal cycle in satellite-derived cloud optical depths (see Boers, R., Ayers, G. P. & Gras, J. L. 1994 Coherence between seasonal variation in satellite-derived cloud optical depth and boundary layer CCN concentrations at a mid-latitude Southern Hemisphere station. *Tellus* **46B**, 123–131).
- T. LENTON (*Plymouth Marine Laboratory, UK*). It is common wisdom amongst sailors when becalmed to motor to the nearest cloud in search of wind. With reference to your figure that DMS flux is positively correlated to sea surface wind speed and that the latent heat of condensation in cloud formation creates winds, what scope is there for a positive feedback between DMS flux from the sea, increased cloud formation, increased winds and therefore an amplification of the sea–air exchange of DMS?
- G. P. AYERS. Your question appears to be based on the premise that there is a connection between an increase in DMS flux leading to an increase in cloud formation. At first order, any change in CCN concentration resulting from a change in DMS flux should not affect the amount of condensable water available for cloud formation, but only affect the number and size of cloud droplets across which that water is distributed. In other words, it is the dynamics of the atmosphere, not a lack of CCN derived from DMS, that defines the rate at which condensable water becomes available for cloud formation, so your suggestion seems unlikely to me.
- The only possibility would be that changes in cloud microphysical properties caused by changes in CCN concentration could have a second order effect on the boundary layer energy and water cycles, and thus possibly the rate of cloud formation, by affecting the drizzle rate (e.g. Boers, R. 1995 Influence of seasonal variation in cloud condensation nuclei, drizzle, and solar radiation, on marine stratocumulus optical depth. *Tellus* **47B**, 578–586).

Discussion

M. H. SMITH (*UMIST, Manchester, UK*). I support your comments on the importance of cloud microphysics on the links between sulphur and climate. However, I have a problem with CCN in that there is no specific supersaturation limit which defines absolutely a CCN. What determines which CCN work to form droplets depends critically upon a complex interplay between atmospheric dynamics and particle concentrations and composition. In a rising parcel of air containing a distribution of particles, it is largely up to the cloud dynamics which particular particles are activated. I note that in your curves of the seasonal variability in CCN concentrations, the amplitude of this diminishes as the supersaturation is reduced.