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**Exploring the Nature of Dimethyl Sulphide  
and its Effects on Cloud Cover in the Great  
Barrier Reef**

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### **Statement of Original Authorship**

The work contained in this thesis has not been previously submitted to meet requirements for an award at this or any other higher education institution. To the best of my knowledge and belief, this thesis contains no material previously published or written by another person except where due reference is made.

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# **Abstract**



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# Chemicals

DMS Dimethyl sulfide.

DMSO Dimethyl sulfoxide.

DMSO<sub>2</sub> Dimethyl sulfone.

DMSP Dimethylsulfoniopropionate.

H<sup>+</sup> Hydrogen.

H<sub>2</sub>O Water.

H<sub>2</sub>SO<sub>4</sub> Sulfuric acid.

MSA Methane sulfonic acid.

MSIA Methane sulphinic acid.

NO<sub>3</sub> Nitrate.

OH Hydroxide.

SO<sub>2</sub> Sulfur dioxide.

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> Ammonium sulphate.

## Chemicals

# Abbreviations

**CCAM** The Conformal-Cubic Amtospheric Model.

**CCN** Cloud Condensation Nuclei.

**CLAW** The Charlson Lovelock Andreae Warren hypothesis.

**CSIRO** Commonwealth Scientific and Industrial Research Organisation.

**CTM** The Chemical Transport Model.

**FT** Free Troposphere.

**GBR** Great Barrier Reef.

**GCM** Global Climate Model.

**GLOMAP** The GLObal Model of Aerosol Processes.

**GLOMAP-mode** The mode seperated version of GLOMAP.

**HYSPPLIT** The HYbrid Single Particle Lagrangian Integrated Trajectory model.

**MBL** Marine Boundary Layer.

**NSS** Non-Sea-Salt.

**PASE** Pacific Atmospheric Sulfur Experiment.

**PBL** Planetary Boundary Layer.

**RCM** Regional Climate Model.

**RH** Relative Humidity.

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## Abbreviations

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**SST** Sea Surface Temperature.

**TAPM** The Air Pollution Model.

**UKCA** United Kingdom Chemistry & Aerosols model.

# 1. Introduction

Climate change is a global issue effecting every country on Earth. The contributions to climate change are varied and complex requiring in depth study to provide as precise a picture as possible. Changes in the Earth's energy balance result from radiative forcing. Radiative forcing is changes in the amount of radiative energy absorbed or reflected by the ground and atmosphere. The radiative forcing component that currently has the largest uncertainty is aerosols (see figure 1.1) (IPCC, 2015). Aerosols are particles suspended in the air that can directly scatter or absorb radiation, or cause water vapour to condense onto them, acting as cloud condensation nuclei (CCN). Clouds formed from CCN reflect radiation back into space. As such the exploration of aerosols as a radiative forcing mechanism is a key area in understanding the larger issue of climate change.

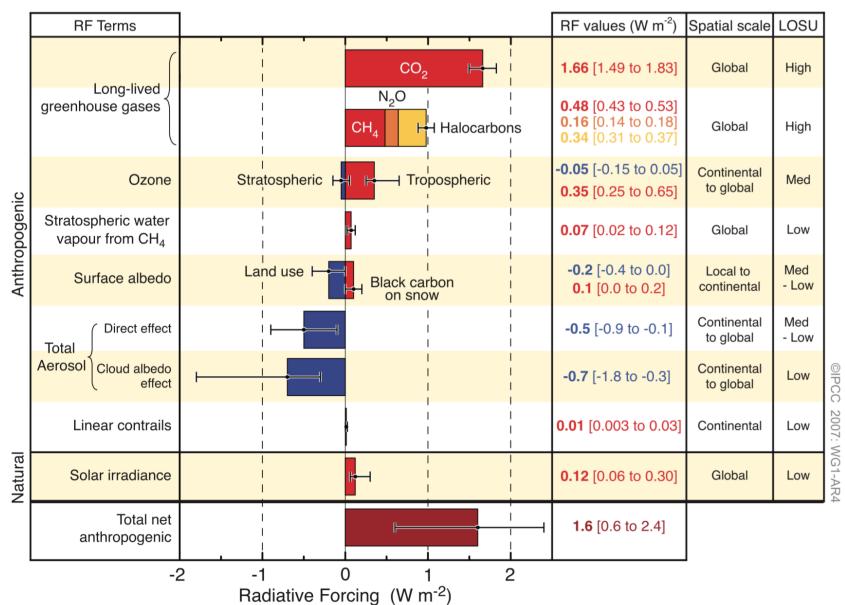


Figure 1.1: A diagram illustrating the various influences on radiative forcing along with their associated uncertainties. From the 2015 Intergovernmental Panel on Climate Change. The largest contributor to uncertainty is currently aerosols (IPCC, 2015).

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A major cause of these uncertainties is the necessity for regionally specific aerosol knowledge (IPCC, 2015). Aerosol composition and concentration differs greatly with changes in sources and atmospheric conditions. This regional variation translates to variation in direct scattering/absorption and cloud producing potential, leading to both local and global effects on climate. Thus it is important to develop tested, regionally specific models that take into account these variations (Cainey et al., 2007; Simpson et al., 2014).

In 1987 the CLAW hypothesis was defined in the seminal paper ‘Oceanic phytoplankton, atmospheric sulphur, cloud Albedo and climate’. The abbreviation CLAW was taken from the initials of that paper’s authors, Robert Charlson, James Lovelock, Meinrat Andreae and Stephen Warren. They proposed a feedback mechanism where stress driven marine biota produced chemicals that influenced cloud cover (Charlson et al., 1987). This paper generated a vast body of research involving many disciplines. Dimethyl sulphide (DMS) is the core chemical responsible for the mechanism and is produced by phytoplankton, and as discovered more recently, coral (Raina et al., 2013). As the climate shifts towards increased temperature, regions like the Great Barrier Reef (GBR) are increasingly losing coral coverage (Hoegh-Guldberg, 1999). It is therefore important to examine the potential effects on climate caused by DMS producing biota undergoing climate related reduction.

Modelling DMS as it is produced, transformed and transported through the atmosphere, in the GBR region, will provide needed insight into the mechanisms surrounding DMS. To do so requires a group of models simulating the different layers of the problem. The bottom most layer is CSIRO’s Conformal-Cubic Atmospheric Model (CCAM) which provides information such as wind speed and temperature (McGregor, 2005). The middle layer is CSIRO’s Chemical Transport Model (CTM) which tracks chemical concentrations (Cope et al., 2009). The final layer is the Global Model of Aerosol Processes (GLOMAP) which simulates aerosol interactions and produces aerosol concentrations. This project will attempt to apply this trio of models, specifically targeting DMS in the GBR region, and to analyse the results with potential for modelling future climate scenarios.

Primarily, it is necessary to understand the role of the atmosphere and its constituents, and where aerosols and DMS are positioned within it. The pathways DMS proceeds down to form CCN involve complicated chemistry (Barnes et al., 2006) and must be explored to ensure the modelling mirrors current theory. The unique climatology of the GBR, including the mechanism and scale with which coral contributes to DMS, needs to be established to provide localised inputs for the group of models. Modelling and the models themselves must be understood to ensure they are being applied

correctly and to determine if they are sufficient for simulating the DMS to CCN pathway. Finally, researching the method through which DMS enters the atmosphere, along with previous DMS to CCN modelling attempts, provides insight into the modelling process and what areas of this research area remain unexplored.

# **Part I**

# **Literature Review**



## 2. Atmosphere

### 2.1 Atmospheric Regions

The Earth's atmosphere is split into a number of different layers. The factor governing their division is the sign of the change in temperature with respect to altitude. For example, in figure 2.2, a decrease in temperature ( $T$ ) with an increase in altitude ( $z$ ) in the troposphere occurs up until the tropopause. The difference in temperature gradients between the different levels of the atmosphere prevent mixing from occurring between layers. This occurs as in most circumstances a parcel of air will rise if  $\frac{dT}{dz} < 0$  and fall if  $\frac{dT}{dz} > 0$ .

#### 2.1.1 Troposphere

The troposphere is the lowest level of the atmosphere sitting between 10 – 15 km above the surface of the Earth. It ends at the tropopause, the first region of constant temperature. The range of altitudes is dependant on time and latitude with the highest region being over the equator, shifting up and down the Earth with its axial tilt (Seinfeld et al., 2012, Chapter 1).

The troposphere is an important region as it contains the majority of the atmosphere's mass (approximately 80 %) and all of its weather. It also contains the highest quantity of water, despite being the smallest region. The layer immediately above the surface of the Earth is called the planetary boundary layer (PBL), or marine boundary layer (MBL) over the ocean (Seinfeld et al., 2012, Chapter 1). The PBL varies greatly in height depending on the surface of the Earth it is over, for example, above the Sahara it can be up to 6 km, while over tropical oceans it is only 100 m (Laing et al., 2011, Chapter 1).

There is a short inversion layer in the troposphere that separates the boundary layer and the free troposphere (FT) (see figure 2.2). It occurs at only a few hundred metres

## 2.1. ATMOSPHERIC REGIONS

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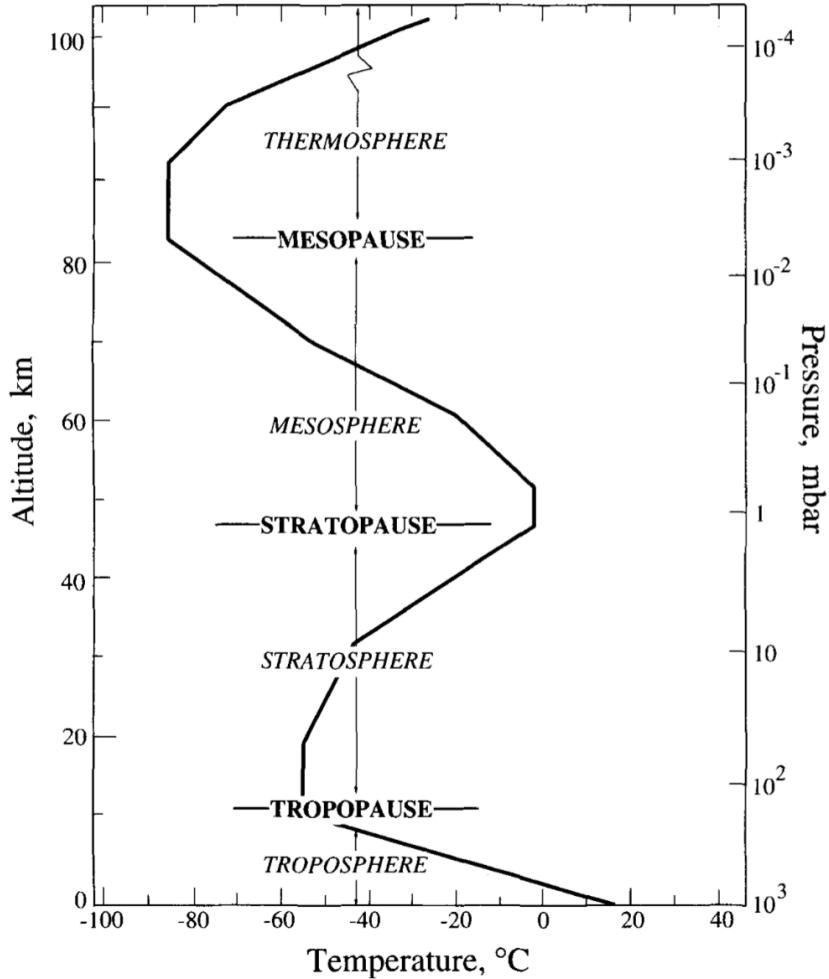


Figure 2.1: The layers of Earth's atmosphere, separated by pauses in temperature change with respect to altitude (Seinfeld et al., 2012, p. 7)

above tropical oceans (Laing et al., 2011). The FT is relatively free of aerosols, as the inversion layer prevents mixing with the boundary layer. Thus there is a low aerosol surface area greatly decreasing heterogeneous nucleation. The inversion layer is not always present, and clouds can breach this layer permitting chemicals access into the FT from the boundary layer. These conditions promote homogeneous nucleation, which is the formation of new particles (Seinfeld et al., 2012, Chapter 8).

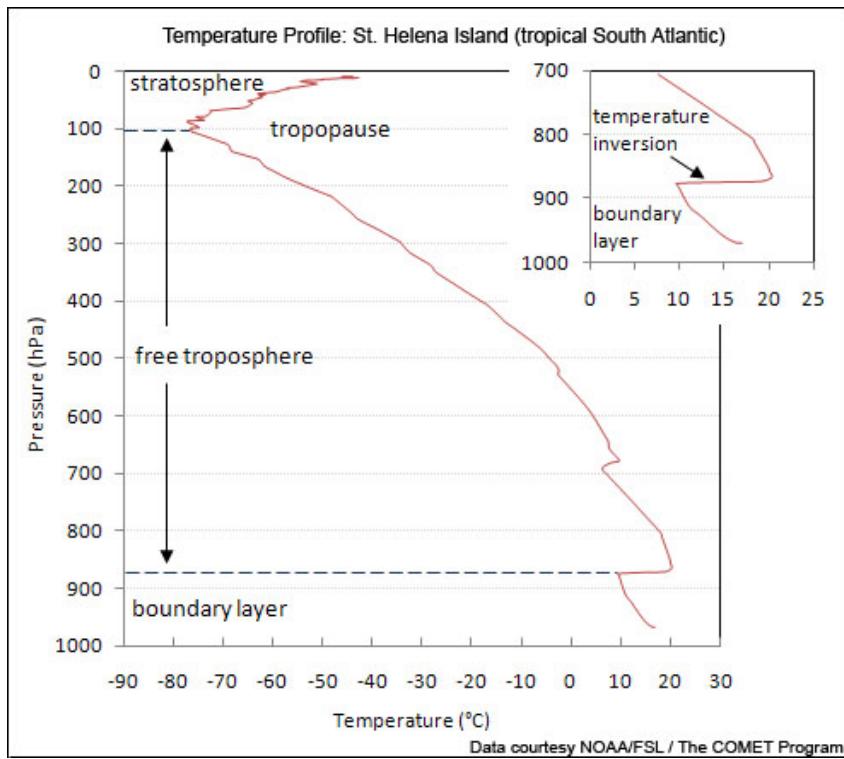


Figure 2.2: An example of the separation between PBL and FT at St. Helena Island. There is an inversion layer present distinguishing the two, however, this obvious separation is not always the case. (Laing et al., 2011, Section 1.5.1)

## 2.2 Relative Humidity and Supersaturation

The amount of water present in air is usually measured via the relative humidity (RH). RH is the fraction of the partial pressure of the gas phase water  $p_{\text{H}_2\text{O}}$  and the saturation vapour pressure for the temperature of the air  $p_{\text{H}_2\text{O}}^0$ , which is the point at which water condenses (Seinfeld et al., 2012, Chapter 1). Supersaturation occurs when there is a RH greater than 100 % (Rogers et al., 1989).

$$\text{RH} = 100 \times \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{O}}^0}. \quad (2.1)$$

When a parcel of moist air rises in the troposphere the temperature within it decreases which increases the RH and a supersaturation can be achieved (Seinfeld et al., 2012, Chapter 1). The temperature decreases due to adiabatic expansion. When this occurs water undergoes spontaneous nucleation onto aerosol particles. A seed particle is required for droplet formation to occur; as homogeneous nucleation

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of water would require a supersaturation far higher than that seen in the atmosphere. CCN are the aerosol seeds that droplets form around (see section 2.4.2). There is therefore a dependence on the level of supersaturation for an aerosol to act as a CCN, which is generally 0.5 – 2 % (Rogers et al., 1989, Chapter 6).

## 2.3 Albedo

The albedo of the Earth is given as the ratio between reflected radiation and incident radiation. The amount of light that is not reflected back into space from the surface of the Earth must be absorbed and thus increases the Earth's temperature. Light may be emitted in the infra-red regime as black-body radiation, which either escapes out into space or is absorbed by greenhouse gases in the atmosphere (Lashof et al., 1990). Water acts as a greenhouse gas, but also acts to increase the albedo of the Earth when formed into clouds. A phenomena that alters the amount of light being absorbed by the Earth is said to exhibit radiative forcing (IPCC, 2015). Aerosols may cause radiative forcing by either directly reflecting or absorbing light, or by assisting in the formation of clouds (Seinfeld et al., 2012, Chapter 4).

## 2.4 Aerosols

An aerosol is any solid or liquid particle suspended in a gas. In the troposphere there is an abundance of aerosols present, with a vast range of sizes and composition.

Aerosols are generally subdivided into modes that indicate their production mechanism. When plotting a property of a large number of particles, such as their number or surface area, against the log of the aerosol diameter, peaks appear at different diameters, which are called modes (Seinfeld et al., 2012, Chapter 8). The modes are nucleation, Aitken, accumulation, and coarse. The diameters over which these modes are generally found in the atmosphere can be seen in figure 2.3.

There are many properties of aerosols that can be examined, such as volume, surface area, mass, chemical composition, hygroscopicity, and concentration. For cloud formation the most important characteristics are hygroscopicity, a measure of the particles ability to absorb water, and particle diameter, which governs whether a particle is large enough to act as a CCN (Rogers et al., 1989, Chapter 6). The number, or concentration, of aerosols is important for cloud formation to an extent. If too many CCN are present the water vapour concentration may not be high enough to form large droplets (Seinfeld et al., 2012, Chapter 22).

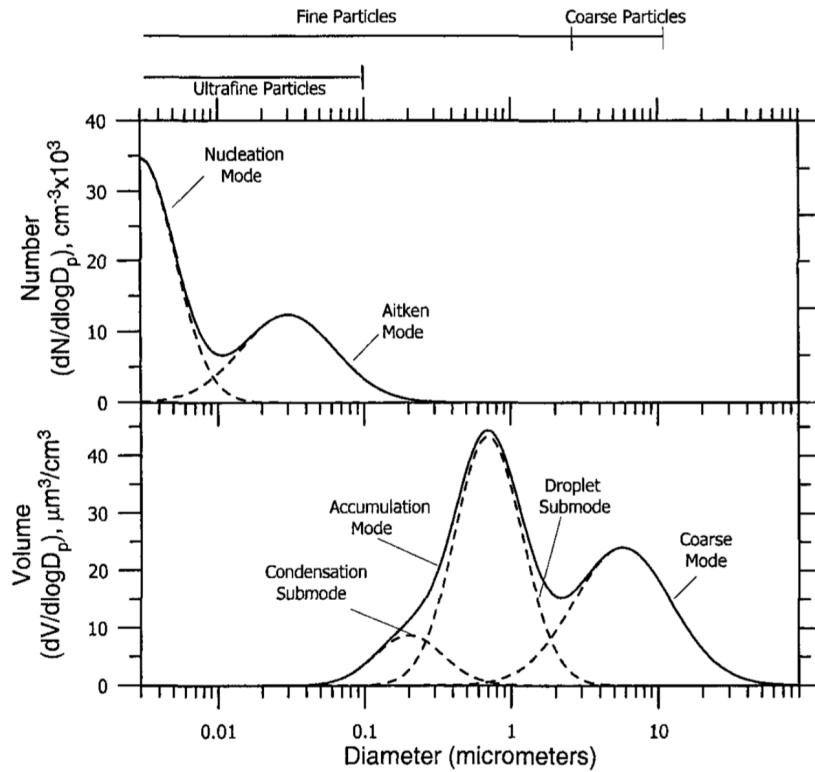


Figure 2.3: An example of the Number and Volume distributions of atmospheric particles indicating the various modes. (Seinfeld et al., 2012, Chapter 8)

The processes that an aerosol undergoes in the atmosphere dictate some of the modes that appear. The nucleation mode arises from particles homogeneously nucleating from a gas, such as sulphuric acid. The accumulation mode is constructed from particles that have condensed vapour such as water, and/or have grown via coagulation, which occurs when multiple aerosol particles stick together. The majority of the accumulation mode peak measured in the atmosphere comes from droplet formation in clouds (Seinfeld et al., 2012, Chapter 8). This droplet sub-mode can be seen in figure 2.3.

#### 2.4.1 Particle Formation

There are two types of aerosols, primary and secondary. The distinction is based on their method of formation.

Primary aerosols are particles that enter the atmosphere directly. In the MBL sea salt particles are an example of primary aerosols (Quinn et al., 2011).

Secondary aerosols are aerosols that have formed in the atmosphere via homogeneous

## 2.4. AEROSOLS

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nucleation. They begin as gases present in high concentrations, in regions with low concentrations of particles, as heterogeneous nucleation is energetically favourable. Creation of secondary particles are dubbed nucleation events, as the atmospheric conditions required for homogeneous nucleation to proceed are uncommon (Seinfeld et al., 2012, Chapter 11).

Because nucleation events are rare and localised in time and space they are difficult to simulate, so the percentage of secondary particles on a global scale has a large uncertainty (IPCC, 2015). Merikanto et al. (2009) modelled global CCN production using the GLOMAP model and showed that between 31 % and 49 % of CCN are secondary particles. Approximately 35 % of these secondary particles were formed in the free and upper troposphere and entrained down into the MBL (Merikanto et al., 2009).

### 2.4.2 CCN

CCN are aerosols that are able to act as sites for the heterogeneous nucleation of water. The water droplets continue to grow by precipitating gas phase H<sub>2</sub>O and eventually become massive enough that they fall out of the sky as rain. The formation of clouds requires CCN, as the atmospheric conditions for homogeneous nucleation of water are never reached. So CCN act as sites for the heterogeneous nucleation of water, forming cloud droplets (Seinfeld et al., 2012, Chapter 17).

CCN are defined for particular supersaturations. This is because whether an aerosol (with a given composition) can act as a CCN, is dependant on the supersaturation of the air it is in. The chemical composition of the particle, or it's hygroscopicity, also affect its ability to act as a CCN. As this information is not always known, empirical equations are often used to describe the concentration of CCN. Take the following equation,

$$\text{CCN}(s) = cs^k. \quad (2.2)$$

Here the concentration of CCN is given as a power function of supersaturation  $s$ , where  $c$  and  $k$  are empirical parameters that conceal the size and composition dependence of CCN. The empirical parameters are sampled locationally with  $c$  varying between 25 – 3500 cm<sup>-3</sup> and  $k$  varying between 0.3 – 1.4 (Seinfeld et al., 2012, Chapter 17). If size distributions, composition and supersaturation are known, then Köhler theory (see section 2.4.3) predicts which aerosols may act as CCN (Rissman et al., 2006).

### Sources and Sinks for CCN

There are a number of CCN sources. Sea salt is an excellent CCN due to its high hygroscopicity (Randles et al., 2004). It is also abundant in atmospheric regions above the ocean and coastline. It is aerosolised by bubble bursting and wind shear at the surface of the ocean.

Chemicals produced by living organisms can pass through a series of chemical reactions and a subsequent nucleation event to produce CCN. An example of this is DMS produced by phytoplankton, which is further explored in chapter 3. An alternative to DMS derived organic aerosols is dissolved organic matter from dying biota collected at the surface that is aerosolised through bubble bursting (Bigg, 2007).

There are also a number of anthropogenic sources of CCN, however, in the Great Barrier Reef region, only sources from shipping exhaust are likely to be of consequence (Fischer et al., 2012).

Aerosols are readily removed from the atmosphere by rainfall and this is even more apparent for CCN as they provide the site of droplet formation. Rain also collects aerosols as the droplets fall (Rogers et al., 1989). Deposition onto other aerosol particles is another way in which CCN may be removed while it is also possible for aerosols to deposit directly onto the surface of the Earth (Seinfeld et al., 2012, Chapter 9).

#### 2.4.3 Köhler Theory

Köhler theory was first described in a paper written by the theory's namesake Hilding Köhler (Köhler, 1936). It provides a model for the growth of existing particles by heterogeneous nucleation. There are two forces influencing this behaviour, the attraction of a molecule's neighbours (the Kelvin effect), and the concentration of the solution (the solute effect) (Rogers et al., 1989).

For a particle of diameter  $D_p$ , the log of the ratio between the water vapour pressure of a droplet and a flat surface is given as a function of the molecular mass of water  $M_w$ , the surface tension  $\sigma_w$ , the gas constant  $R$ , the temperature  $T$ , the water density  $\rho_w$ , and the number of moles of the solute  $n_s$ .

$$\ln \left( \frac{p_w(D_p)}{p^\circ} \right) = \frac{4M_w\sigma_w}{RT\rho_w D_p} - \frac{6n_s M_w}{\pi \rho_w D_p^3}. \quad (2.3)$$

## 2.4. AEROSOLS

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Substituting in the known constants produces  $\frac{4M_w\sigma_w}{RT\rho_w} \approx \frac{0.66}{T}$  and  $\frac{6n_s M_w}{\pi\rho_w} \approx \frac{3.44 \times 10^{13} v m_s}{M_s}$  with units  $\mu\text{m}$  (Seinfeld et al., 2012, p. 770). The moles of solute  $n_s$  is given by the ratio between the number of ions per molecule  $v$ , the solute particle mass  $m_s$  and the solute molar mass  $M_s$ . Substituting into equation (2.3) gives,

$$\frac{p_w(D_p)}{p^\circ} = e^{\frac{0.66}{T D_p}} e^{-\frac{3.44 \times 10^{13} v m_s}{M_s D_p^3}}. \quad (2.4)$$

Here the first exponential term represents the Kelvin effect and the second represents the solute effect.

Plotting equation (2.4) produces Köhler curves that show, for an initial dry particle size, the required supersaturation for particle growth to occur even as the particle itself grows and changes concentration. An example of Köhler curves for different seed diameters of ammonium sulphate  $(\text{NH}_4)_2\text{SO}_4$  can be seen in figure 2.4. Here, equation (2.4) has been plotted with  $v = 3$ ,  $M_s = 132.14 \text{ g mol}^{-1}$ .

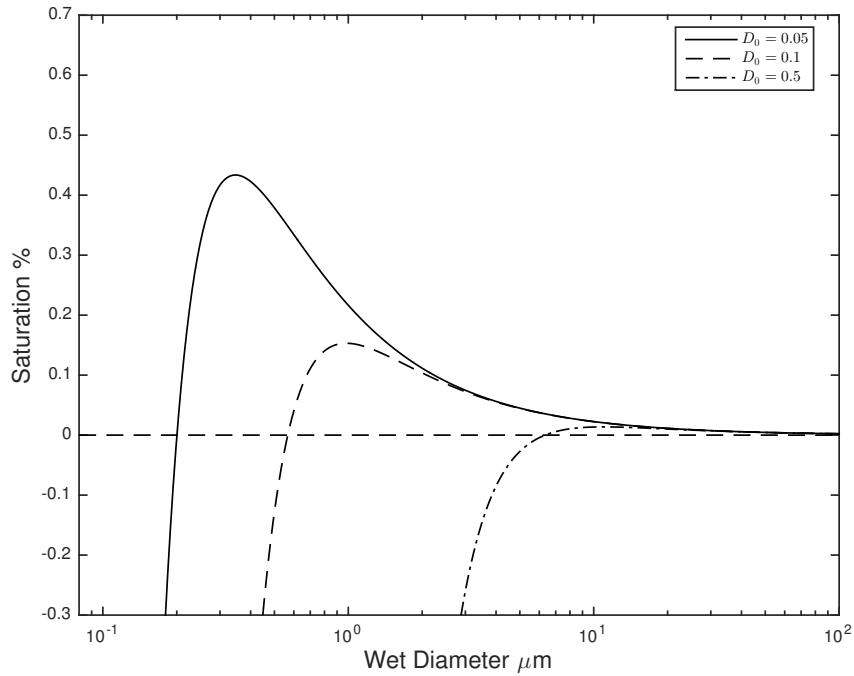


Figure 2.4: The Köhler curves for ammonium sulphate  $(\text{NH}_4)_2\text{SO}_4$  for three dry diameters  $0.05, 0.1, 0.5 \mu\text{m}$  using approximations from Seinfeld et al. (2012, p. 770)

There are a number of variations to the general form of the Köhler curve equation that deal with alternate conditions, such as insoluble seed particles, and mixes of soluble and insoluble seeds (Seinfeld et al., 2012, Chapter 17).

## 3. Dimethyl Sulphide

Dimethyl sulphide (DMS) is a naturally produced chemical that has been theorised to influence cloud coverage and potentially act as a negative feedback mechanism for climate change (Charlson et al., 1987). DMS enters the atmosphere and goes through an array of chemical reactions to produce sulphuric acid ( $H_2SO_4$ ) (Barnes et al., 2006), which may then nucleate into aerosols that can act as CCN. Measurements of aerosols in the atmosphere, particular remote marine areas show a large percentage being of the non-sea salt sulphate variety, potentially sourced from DMS (O'Dowd et al., 1997).

### 3.1 Chemistry

The chemical processes that DMS and dimethyl sulfoxide DMSO undergo in the atmosphere are extremely complicated with many competing pathways (see figure 3.2). Barnes et al. (2006) have reviewed the extensive literature on this subject, with great detail. They split the problem into three sections, the first, DMS reactions and products, the second, DMSO reactions and products, and the third, multiphase chemistry of the DMS pathways.

The reaction processes for DMS are reactions with the OH radical, the  $NO_3$  radical, and with Halogen Atoms and Oxides. During the day the dominant reaction is the addition pathway through OH, while at night it is the abstraction pathway through  $NO_3$  as seen in figure 3.2 (Barnes et al., 2006). Pathways involving halogen species are generally ignored in modelling due to low availability, though levels of hypobromite high enough to be influential have been measured in the troposphere (Platt et al., 2003).

DMSO appears to be the major product of DMS oxidation in the atmosphere. Its reactions are the same as for DMS listed above. The atmospheric lifetimes calculated indicate that OH radicals dominate reactions for DMSO (Barnes et al.,

### 3.1. CHEMISTRY

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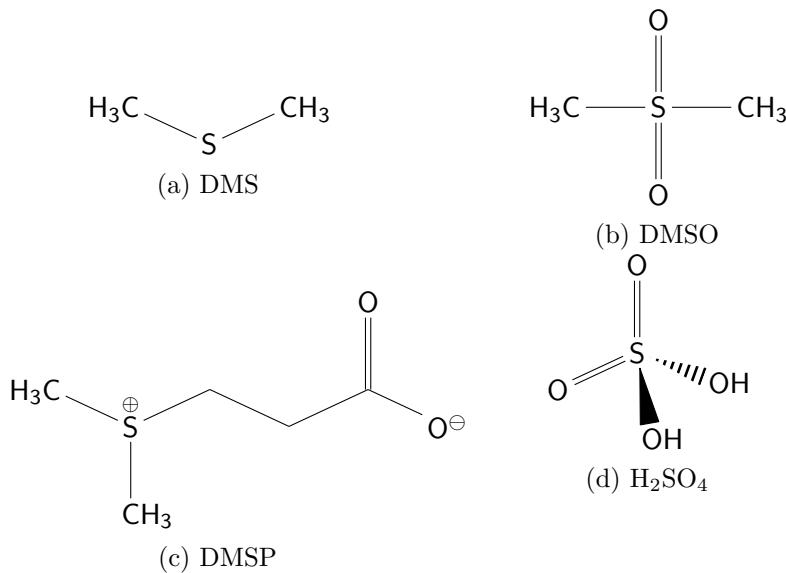


Figure 3.1: The chemical structure of important chemicals relating to DMS

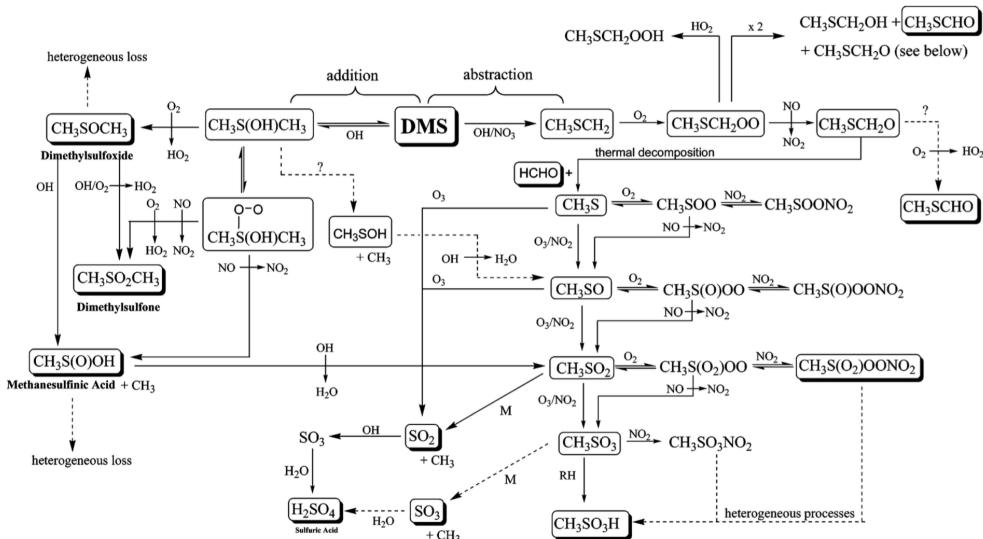


Figure 3.2: The reaction scheme for DMS oxidised by  $\text{NO}_3$  and  $\text{OH}$  radicals (Barnes et al., 2006).

2006). Methane sulphinic acid (MSIA) is a product of this reaction, which goes on to form methane sulphonic acid (MSA). DMSO<sub>2</sub> is also a product of this reaction and was considered the most prevalent pathway, but Barnes et al. (2006) found instead that the MSIA pathway heavily dominates. SO<sub>2</sub> is the largest possible outcome of MSA oxidation.

### 3.1.1 Multiphase Chemistry

The pathways examined in the preceding section are for gas phase reactions. However the atmosphere also contains liquid water in the form of droplets leading to aqueous phase reactions. The difference between gas and aqueous phase reactions is largely due to the availability of  $\text{H}_2\text{O}$  and  $\text{H}^+$  (Barnes et al., 2006). A combination of the two, multiphase chemistry, is needed. Interestingly, DMS is not as soluble in water as DMSO,  $\text{DMSO}_2$ , MSA and MSIA so its multiphase reactions are not as important.

Barnes et al. (2006) have analysed the multiphase chemistry of all five chemicals and recommend that modellers implement the multiphase chemistry they have illustrated. They include a list of aqueous phase rate coefficients for the five chemicals of major interest, though do not consider a coupling of the gas and aqueous-phase systems necessary. Jacob (2000) provides a method for calculating chemical uptake by aerosols, while Henry's law is recommended for calculating concentrations, as an approximation.

## 3.2 Dimethyl Sulphide, Aerosols and the Environment

### 3.2.1 The CLAW Hypothesis

In the CLAW hypothesis DMS produced by phytoplankton in the ocean was considered as the precursor for CCN in the MBL. The CCN produced were investigated for their cloud producing properties and the subsequent change in planetary albedo. The feedback loop, as seen in figure 3.3, was closed by linking the DMS precursor dimethylsulphoniopropionate (DMSP) to a survival trait of the phytoplankton.

Anthropogenic sources were ignored as the regions the hypothesis focussed on were remote, while other natural gaseous sulphur producers were considered insignificant. The purpose for phytoplankton's production of DMS was suggested to be from DMSP, used in osmo-regulation and the cycle for methionine (Vairavamurthy et al., 1985). The highest flux of DMS from the ocean to the atmosphere was concluded to occur in the most saline, hottest and sunlit areas. The formation of sub-micrometer NSS sulphate particles was attributed to the oxidation of DMS by hydroxide. Other reactions removing DMS to non CCN forms were considered too low to have a significant effect. From here it was concluded that increases in DMS flux from the ocean directly increased the number of CCN present in the form of NSS sulphate aerosols (Charlson et al., 1987).

### 3.2. DIMETHYL SULPHIDE, AEROSOLS AND THE ENVIRONMENT

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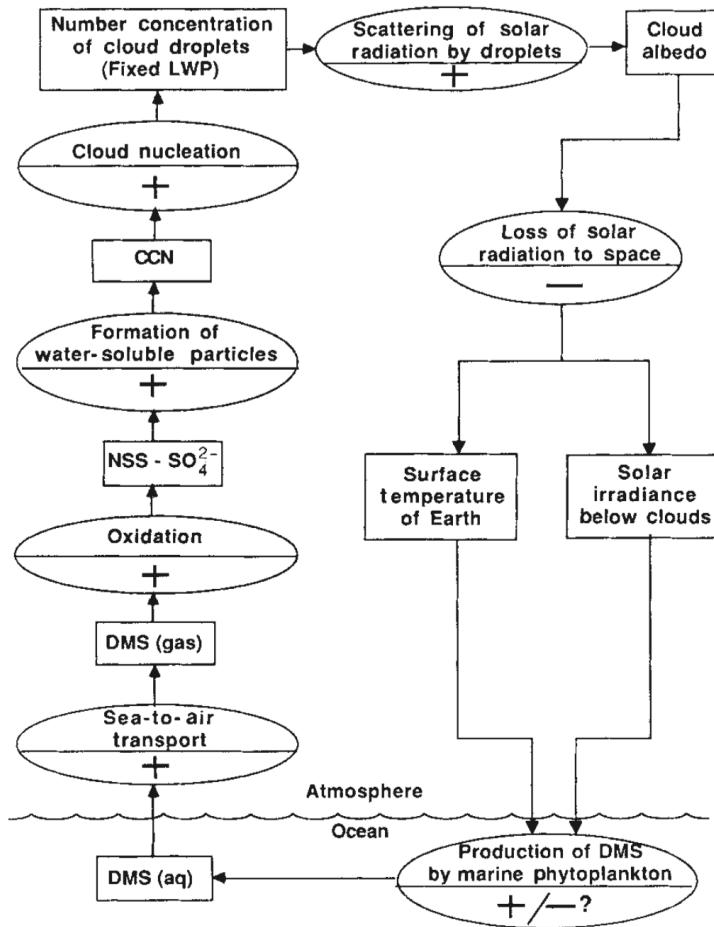


Figure 3.3: The original feedback loop diagram describing the CLAW hypothesis postulated in the paper by Charlson et al. (1987). Rectangles are measurable variables, ovals are processes. The sign indicates the effect a positive change in the previous rectangle has on the next rectangle. The appearance of both signs in the production of DMS oval reflects the author's uncertainty of this particular effect. If it is positive, then the diagram describes a negative feedback loop, stabilising the climate.

Charlson et al. (1987) attempted to establish NSS sulphate as the prominent CCN in the remote marine atmosphere and that higher concentrations increased or altered the reflective properties of cloud cover and thus albedo. NSS sulphate particles derived from DMS were considered to be in the right size range and have the correct properties for acting as CCN. They used a model developed by Twomey (1977) to predict the change in albedo from the change in the number of CCN. By keeping the water content constant and increasing the number of CCN, the mean radius of the droplets formed decreased. However the overall surface area of the droplets increased, thereby increasing cloud albedo. The model was used along with top of cloud satellite data to predict a change of 0.016 to planetary albedo from a 30 %

increase in CCN.

The final part of the loop involved the DMSP production mechanism and an attempt to link phytoplankton species that emit large amounts of DMSP with increased survival. A number of possible explanations were put forward, such as increased ocean salinity during ice ages, as DMSP protects against dessication. The resulting accidental formation of CCN may have acted as a further survival mechanism. This completes the hypothesis that a negative feedback mechanism exists where increases in the Earth's temperature increases planetary albedo which then decreases the Earth's temperature (Charlson et al., 1987).

An analysis of aerosol data collected at Cape Grim in Tasmania was one of the first attempts to experimentally validate the CLAW hypothesis (Ayers et al., 1991). Ayers et al. (1991) compared concentrations of methane sulphonic acid (MSA) and concentrations of CCN. MSA was considered a relevant surrogate for DMS in the absence of long term DMS data. The results showed a correlation between MSA and CCN concentrations along with seasonal dependence. Interestingly, there was a period during winter where MSA dropped close to zero while CCN did not, indicating the presence of an unknown CCN source. The relationship between MSA and CCN was found to be non-linear. This experiment showed that the production of CCN from phytoplankton aspect of the CLAW hypothesis was at least plausible.

### 3.2.2 Post-CLAW Research

The CLAW hypothesis has prompted a large amount of research and experimentation. Quinn et al. (2011) explored this research and formed the view that the hypothesis has been invalidated. The three core elements of the CLAW hypothesis were identified as follows: a significant proportion of CCN in the MBL must be DMS derived, changes in DMS derived CCN cause changes to cloud albedo, and DMS production is affected by ocean surface temperatures and solar radiation changes due to cloud albedo (Quinn et al., 2011). The final cycle proposed by Quinn et al. (2011) can be seen in figure 3.4.

Quinn et al. (2011) identified two primary CCN competitors, sea salt particles and primary organic particles. A significant amount of MBL CCN were found to have a sea salt nucleus. Experiments where particles were heated past 600 °C reported 20 % refractory particles sourced at 400 m across the Atlantic, and 40 % aboard a research ship in the north-east Atlantic. Sea salt particles are likely to be the only refractory particles present (O'Dowd et al., 1993). Sea salt particles were also found to make up 60 % of evaporated cloud droplets. The difference in these percentages is because

### **3.2. DIMETHYL SULPHIDE, AEROSOLS AND THE ENVIRONMENT**

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sea salt particles act as CCN at lower supersaturations (Tang et al., 1997).

Primary organic particles are aerosolised through the same mechanism as sea salt, but the constituents come from the detritus of organisms which collects on the ocean surface. The larger organic particles may break up in the atmosphere due to UV exposure or acidification. According to measurements recorded in the North Atlantic ocean, mass concentration of these particles increased during bloom periods (O'Dowd et al., 2004). Organic particles (and sea salt) may also scavenge DMS products, which removes their effect on CCN concentrations, if the scavenging particle was already acting as a CCN. Due to the seasonal nature of primary organic particles, they may account for some of the seasonal relationship originally found by Ayers et al. (1991), between DMS and CCN concentrations.

For the remaining DMS derived particles, direct nucleation of DMS products likely occurs at the top of clouds, in the FT. Clouds remove existing particles in this region, which decreases the available surface area, and promotes homogeneous nucleation (Perry et al., 1994). Deep convective clouds also move DMS up into the FT (A. Clarke et al., 1998). The faster winds present in the FT would move the particles away from the DMS's origin, breaking the localisation required for the feedback loop. Quinn et al. (2011) argues that the majority of DMS derived particles present in the MBL are from this process.

Cainey et al. (2007) similarly identified three main ideas through which the feedback mechanisms of the CLAW hypothesis have been diminished. These are: the effectiveness of DMS to become CCN, the prevalence of sea salt particles in the CCN size range, and the direct aerosolisation of organic particles from the ocean surface through bubble bursting.

The effect that aerosols have on cloud albedo is more complicated than the direct relationship proposed in the original CLAW hypothesis (Quinn et al., 2011; Cainey et al., 2007). An increase in cloud albedo can be countered by a decrease in cloud fraction through improved entrainment of sub-saturated air around the cloud (Zuidema et al., 2008). Charlson et al. (1987) predicted a 1.3 °C decrease in surface temperature for a 30 % increase in CCN. As the extra CCN are unlikely to be entirely DMS derived, the required increase in DMS flux would need to be very high, around 300 % according to values modelled by Woodhouse et al. (2010).

An alternative action through which DMS derived sulphur compounds are removed, and thus prevented from becoming CCN directly, is through heterogeneous nucleation onto existing particles (Cainey et al., 2007). Such an action may work to alter the chemistry of the particle and thus the albedo of the clouds formed from them. This

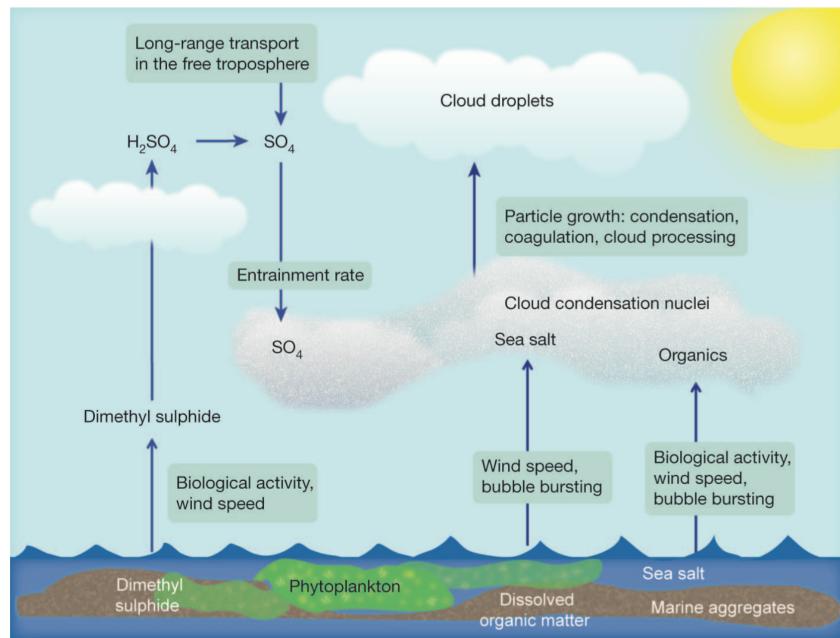


Figure 3.4: An updated cycle for CCN production in the MBL. Major changes to the cycle in figure 3.3 are nucleation in the FT driven by clouds, and the presence of sea salt and primary organic aerosols (Quinn et al., 2011).

may provide an alternate way for DMS to affect climate.

Quinn et al. (2011) advise that the CLAW hypothesis should be retired, but acknowledge its impact in developing this area of science. Other mechanisms of climate regulation may still be present, such as sea salt particle concentration increases with wind speed, and primary organic particles with biological production. Cainey et al. (2007) take a more compromising stance, advising that research into the CLAW hypothesis is still on-going and current results need to be fully implemented in modelling.

### 3.2. DIMETHYL SULPHIDE, AEROSOLS AND THE ENVIRONMENT

## 4. The Great Barrier Reef

The Great Barrier Reef (GBR) is the world's largest organic structure. The marine park encompassing it is 344 400 km<sup>2</sup> (see figure 4.1), of which around 6 % is comprised of 2900 separate coral reefs (Borthwick et al., 2006).

Climate change is causing an increase in sea surface temperature (SST), which effects coral survival in the GBR (Hoegh-Guldberg, 1999). Most corals rely on a symbiotic relationship with algae for energy, but when sufficiently stressed, the algae is ejected, this is coral bleaching (Hoegh-Guldberg, 1999). Stresses associated with changing conditions, and bleaching events, may also impact coral's production of DMS (Raina et al., 2013).

Satellite imagery has been used to try and establish a link between SST and cloud coverage in the GBR. Leahy et al. (2013) found relationships where changes in SST was responsible for changes in cloud cover, but also that cloud cover was responsible for changes in SST. Both were found to have a three day delay. The SST to cloud cover correlation implies a negative feedback mechanism for cloud formation, with DMS produced by stressed coral mentioned as a possible source (Leahy et al., 2013).

### 4.1 Coral DMS Production

While the CLAW hypothesis was based only on phytoplankton as a producer of DMS, phytoplankton are not the only organisms responsible for its production. DMSP production by coral is another source. Research has been performed on the effects of ocean temperature changes (G. Jones et al., 2007), and the role of Symbiodinium (the algae that lives inside coral in a symbiotic relationship) in DMSP production (Raina et al., 2013). DMSP is converted to DMS by bacteria in the ocean (Todd et al., 2007).

Separate research on DMSP production by Symbiodinium, and adult coral, had

## 4.1. CORAL DMSP PRODUCTION

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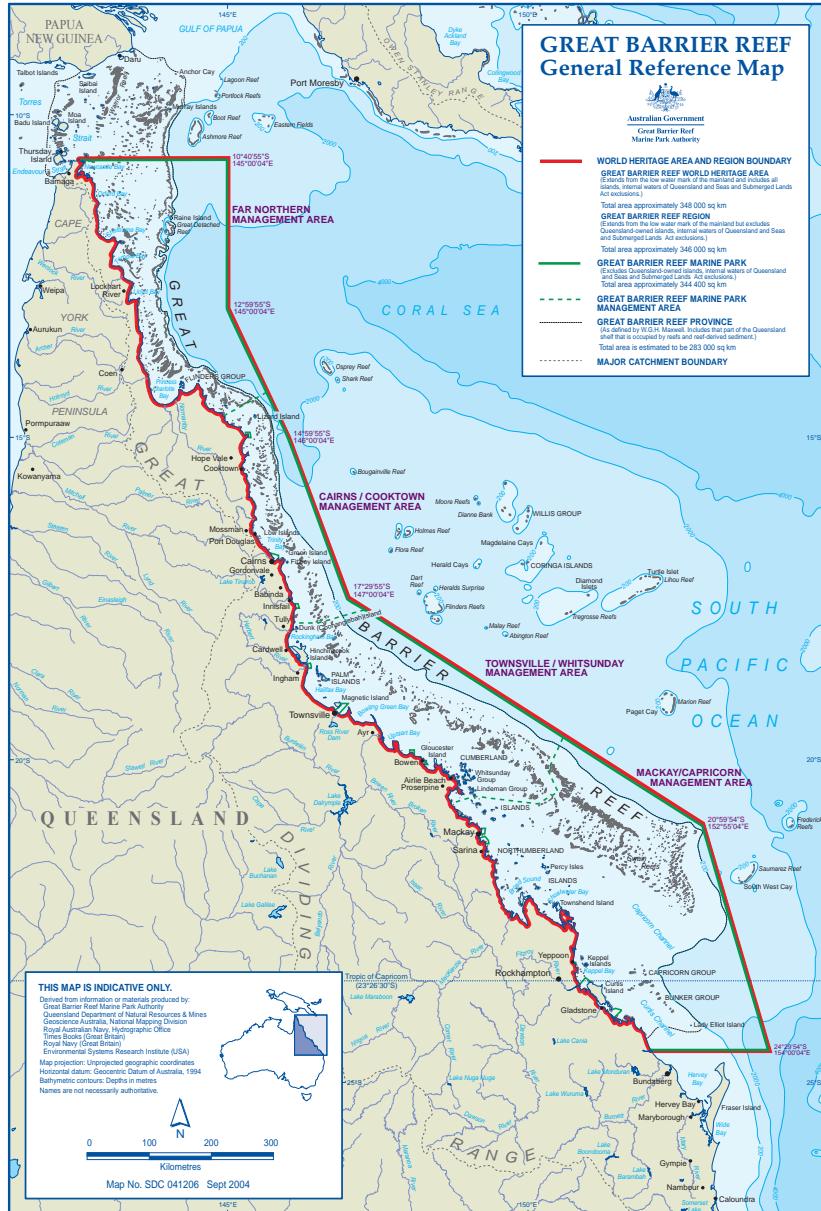


Figure 4.1: The boundary of the Great Barrier Reef Marine Park illustrating the extent of its coverage along the Queensland coast (Borthwick et al., 2006).

previously shown a discrepancy in total DMSP production. Experimentation on the larval phase of coral yet to be inhabited by Symbiodinium has shown that coral larvae produce DMSP independently (Raina et al., 2013). DMSP concentration from coral was also found to be two times higher than that produced by benthic algae common to the GBR (Raina et al., 2013).

An increase in temperature has been found to result in an increase in coral DMSP production (see figure 4.2). DMS is known to have antioxidative effects, implying that increased DMSP production is a defence against damage caused by heat stress. Adult colonies whose Symbiodinium was destroyed by heat stress also produced increasing levels of DMSP with increasing temperatures. Prior to Raina et al. (2013), it was assumed that increasing temperatures killing off the Symbiodinium would quickly decrease DMSP production. This no longer appears to be the case.

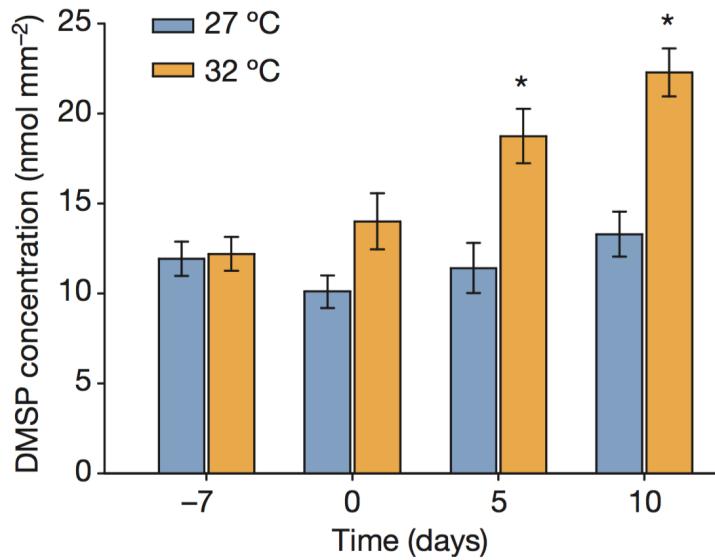


Figure 4.2: Adult coral DMSP production increases when stressed by a higher temperature over an extended time period (Raina et al., 2013).

If DMSP concentration has a resulting effect on cloud formation through CCN, changing coral cover due to changing climate may impact local climate regulation.

## 4.2 GBR DMS Production

Coral's eventual production of DMS in the GBR region has been explored experimentally. Results from the GBR indicate that corals can produce very high concentrations of DMS and DMSP (Broadbent et al., 2004). These concentrations also appear to depend on SSTs, and on tidal levels (G. Jones et al., 2007). The extent of the GBR presents a large source of sulphur that enters the atmosphere (G. B. Jones et al., 2005).

The GBR region is exposed regularly to south-easterly and southerly trade winds, providing the wind shear required to transfer DMS from the ocean to the atmosphere

## 4.2. GBR DMS PRODUCTION

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(Liss, 1983). During a voyage in 1997, G. B. Jones et al. (2005) measured the highest levels of atmospheric DMS when these trade winds passed over large areas of the reef experiencing low tides (see figure 4.3).

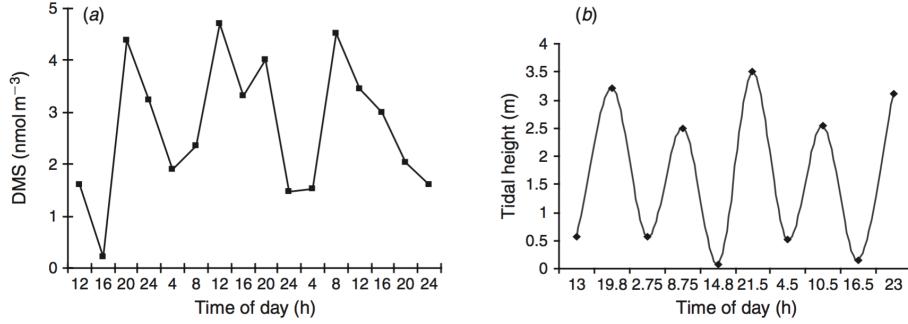


Figure 4.3: Data indicating the presence of a delayed link between atmospheric DMS concentrations and low tide events in the northern GBR and NW Coral Sea (G. B. Jones et al., 2005).

From here the production of CCN from GBR sourced DMS is not as well established. Much depends on the meteorology of the region and the relative concentrations of competing CCN and DMS sinks. Localised modelling is needed to provide predictions in this area of research (Cainey et al., 2007).

## 5. Modelling

The complexity of the atmosphere and the processes within it, detailed in chapter 2, require modelling to produce theoretical descriptions of the systems. Generally, a number of models are chained together to simulate different parts of the climate system. Each of these models is built upon a number of theories that are used depending on the state of the system at the time (Jacobson, 2005, Chapter 21). This complexity makes atmospheric modelling difficult and broad. Fortunately many models have been developed around the world to fill niches such as HYSPLIT for trajectory modelling, the Unified Model for climate and weather modelling and CCAM for atmospheric modelling (Draxler et al., 1997; Mann et al., 2010; Cope et al., 2009; McGregor et al., 2008).

The first choice to make when deciding which model to use is between a Global Climate Model (GCM) and a Regional Climate Model (RCM). The difference is in the granularity achieved in the discretisation used to solve the governing equations, and the requirements of boundary conditions (Thatcher et al., 2015). A RCM is run on a smaller scale for a specific region with a high density of grid points. As only a small portion of the Earth's surface is simulated, the values of parameters at the boundary of that region must be known in advance (Hurley, 2002). Usually these boundary conditions are obtained from a previous run of a GCM. Although a GCM is less restrictive than a RCM, its lack of high resolution may miss small but critical details. Conversely, the regional restriction of a RCM can miss distant events that may influence the climate in the simulated region (Seinfeld et al., 2012, Chapter 25).

### 5.1 Back Trajectory Modelling

When working in atmospheric science, it is often necessary to model the trajectories that parcels of air travel. With the advent of large scale meteorological measurements, the data required to model this process is now being produced. Trajectory modelling

## 5.2. CCAM, CTM, GLOMAP

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is able to take a particular location and predict, forward or backward in time, the path a parcel of air travels to or from that location. It can be used to predict whether air at a particular location has passed over a region or event of interest or, for example, whether there has been contamination from anthropogenic sources (Draxler et al., 1998).

HYSPLIT is the Hybrid Single Particle Lagrangian Integrated Trajectory model developed by the National Oceanic and Atmospheric Administration and Australia's Bureau of Meteorology. It takes as input a variety of different meteorological data sources to produce the field the parcel travels through. HYSPLIT's efficacy in performing back trajectory modelling is well established (Draxler et al., 1998). It has been used to model many different scenarios from forecasting fire smoke movement (Glenn D Rolph et al., 2010) to nuclear cloud dispersion (G D Rolph et al., 2014).

A Lagrangian model may be implemented in two different ways. A puff model regularly releases and follows a parcel of air containing the required fraction of trace components. The puff moves and expands depending on advection and diffusion respectively. A particle model releases many single particles which are moved through advection, but which are also randomly moved based on the diffusion present (Draxler et al., 1997). HYSPLIT implements a hybridisation of these models by using the particle style for vertical motion, and the puff style for horizontal motion (Hurley, 1994).

HYSPLIT, like all atmospheric models, is sensitive to initial conditions (Challa et al., 2008) and its accuracy is dependent on the error margins of the meteorological data it makes use of (Draxler et al., 1998). The results of any trajectory run are therefore less accurate the further away from the initial conditions the trajectory gets. There is also a dependence on the spatial and temporal granularity of the meteorological data. As such, HYSPLIT offers the ability to slightly permute the initial conditions of the model to produce a multitude of possible trajectories for a single location and time (Draxler et al., 1997). It is also possible to produce multiple trajectories over time or over space and a robust scripting platform exists to allow this (Draxler et al., 1997).

## 5.2 CCAM, CTM, GLOMAP

The three models to be used in this project are CCAM, CTM and GLOMAP-mode. CCAM provides the meteorological data needed for CTM and CTM provides the

chemical concentration data required for GLOMAP-mode. However, currently the system is limited to running CCAM offline from the other models (see figure 5.1) (McGregor et al., 2008). Thus there is no feedback into the meteorology from changes in aerosol levels, such as cloud production caused by changes in CCN concentrations.

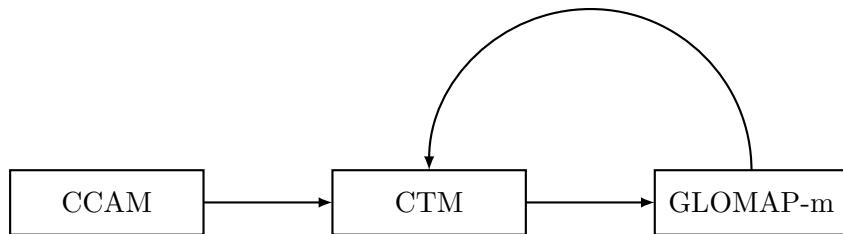


Figure 5.1: The group of models prepared by CSIRO for modelling from meteorology to aerosols. Arrows indicate the direction data passes.

This combination of models has been used previously in the Sydney Particle Study (Cope et al., 2014). The Sydney Particle Study was a large scale study performed by seven different organisations and lead by CSIRO. It encompassed both measurement and modelling of fine particles in the Sydney area, with a view to understand their exposure to Sydney's population. Both CCAM and TAPM (an alternative meteorological model produced by CSIRO) were used as the RCMs for the study. Their outputs were compared with each other, and with the collected data. CTM, and consequently GLOMAP-mode, were used for the particle dynamics and chemical transport modelling within the two RCMs. Both RCMs performed well, with predictions of sea salt, organic matter and secondary inorganic aerosols within 15 % of observations (see figure 5.2) (Cope et al., 2014).

### 5.2.1 CCAM

CCAM is CSIRO's Conformal-Cubic Atmospheric Model. Most RCMs are performed on a grid that simulates only the area of interest, requiring spatial boundary conditions to be fed into the model at each time step (Hurley, 2002). Because of CCAM's approach of conformal cubic mapping, the majority of grid points can be focussed onto the region of interest while still simulating the rest of the globe with a gradient of accuracy (see figure 5.3). This removes the necessity for boundary conditions as the full globe is being simulated. This allows distant events to influence the region of interest. However, there are fewer grid points in distant regions, sacrificing accuracy for computation time (McGregor, 2005).

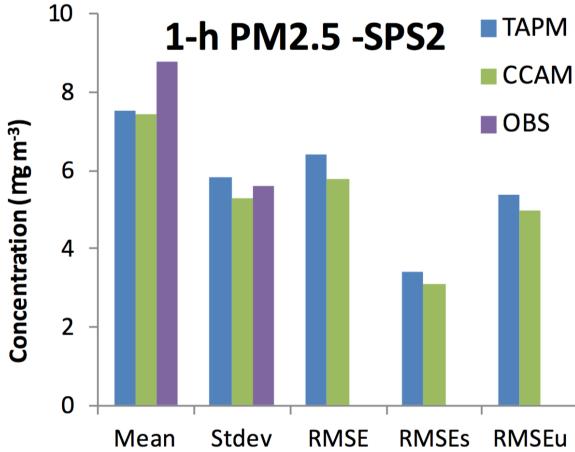


Figure 5.2: The hourly averaged concentrations of PM2.5 particles for the second Sydney Particle Study. Both CCAM and TAPM used as the base meteorological model produce similar average concentrations, close to observation (Cope et al., 2014).

As inputs CCAM can accept data sets from a GCM and nudge the model towards these values (McGregor, 2005). Although work is being done to incorporate a coupled ocean model with matching grid structures, without this the oceanic parameters, such as sea surface temperature, must be input as both spatially and temporally varying maps (McGregor et al., 2008). Despite the non-uniformity of the cubic grid structure, CCAM produces latitude and longitude based output through interpolation of the cubic grid data (Thatcher et al., 2015).

The current implementation of CCAM uses a semi-Lagrangian solver that is semi-implicit and non-hydrostatic, programmed in FORTAN. The solver is designed for expansion to a large number of cores, while dealing with the singularity-like points caused by the cubic mapping (Thatcher et al., 2015). It is also possible to run the model multiple times, focussing the grid in at each step while nudging is performed using the previous runs' data (McGregor et al., 2008).

### 5.2.2 CTM

CTM is the Chemical Transport Model produced at CSIRO. It deals with various transport processes relating to chemicals found in the atmosphere, as well as deposition onto particles, changes in chemical structure, and emission sources (Cope et al., 2009). It uses a regular grid structure which requires boundary conditions (see figure 5.4) that are usually taken from a GCM (Cope et al., 2014). The transport of each chemical species is modelled using an advection diffusion equation around the

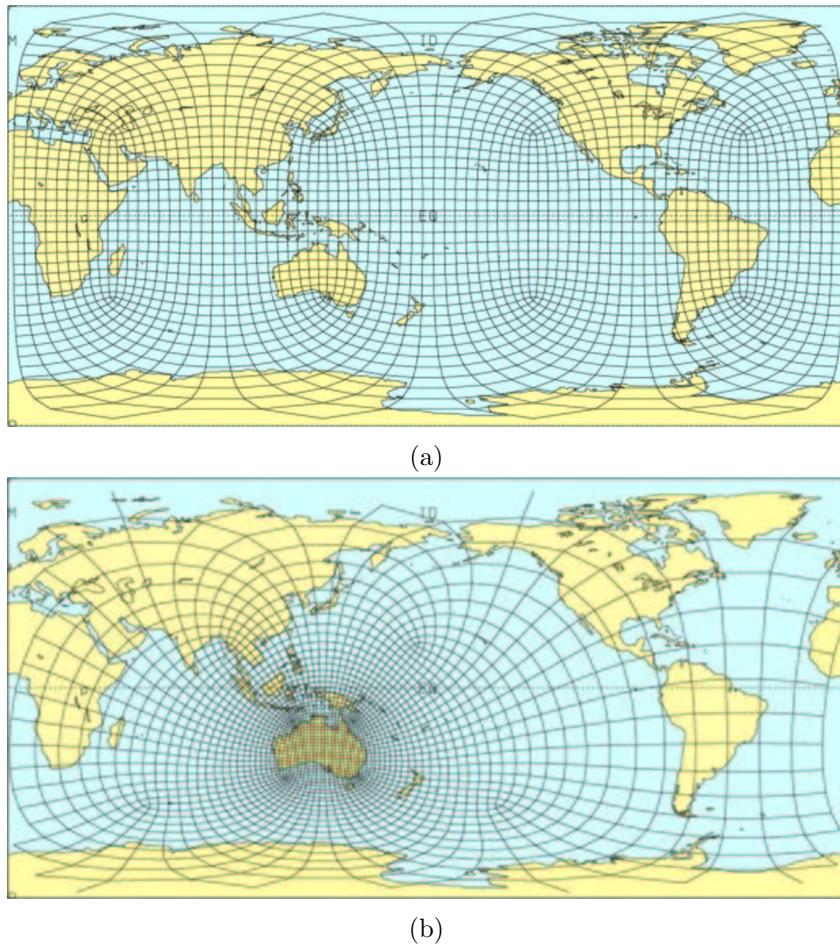


Figure 5.3: Two examples of the conformal cubic mapping, used by CCAM, showing both a focussed and unfocussed transformation of the grid (McGregor, 2005).

chemical's concentration, with source terms relating to different chemical processes. Each of these are themselves modelled and solved before being fed back into the advection diffusion solver (Cope et al., 2009).

CTM is written in FORTRAN, but allows for chemical reactions to be entered as regular form chemical equations (Cope et al., 2009). It requires a meteorological map as input, along with initial and boundary conditions for each chemical being tracked. Maps for the introduction of chemicals from the surface to the atmosphere are also required, such as when DMS is produced by the GBR. CTM outputs atmospheric maps of chemical concentrations.

## 5.2. CCAM, CTM, GLOMAP

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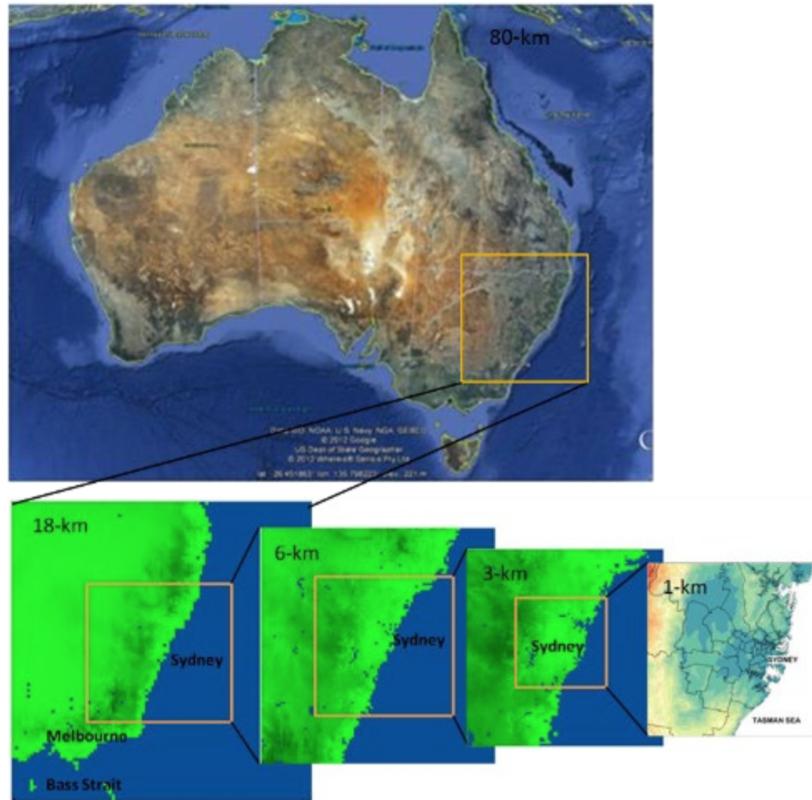


Figure 5.4: A series of the zooming CTM grids used in the Sydney Particle Study. An example of a CTM produced chemical concentration map can be see at the bottom right (Cope et al., 2014).

### 5.2.3 GLOMAP and GLOMAP-mode

GLOMAP is the aerosol micro-physics component of the UKCA model developed at Leeds university. It uses atmospheric information and chemical concentrations to simulate the large amount of interactions aerosols undergo. It models new particle formation, condensation, cloud processing, hygroscopic growth and many other aerosol processes (Mann et al., 2010).

GLOMAP-mode is an alternate version of GLOMAP which segregates aerosols via modes (see section 2.4) rather than the GLOMAP's direct bin approach. GLOMAP-mode also uses the equilibrium Henry's law style aqueous phase reactions recommended by Barnes et al. (2006), while GLOMAP uses a more computationally expensive diffusion limited method (Mann et al., 2010). Both differences make GLOMAP-mode less accurate, but also less computationally expensive. Some treatments of particles are also adjusted to better make use of the modal structure. An example is that GLOMAP applies rain-out to any particles over 103 nm, while GLOMAP-mode applies rain-out to soluble particles in the accumulation and coarse

modes (Mann et al., 2010). For modelling DMS and its aerosol products, GLOMAP uses the sulphur oxidation steps outlined in Seinfeld et al. (2012) and precomputed Henry's law coefficients (Mann et al., 2010).

The chemical concentration maps needed to feed into GLOMAP can either be offline, computed beforehand, or online (Mann et al., 2010). Online maps are updated by what is consumed or produced within GLOMAP and then passed to a chemical transport model running above GLOMAP (Spracklen et al., 2003). GLOMAP produces maps of aerosol concentrations, separated into bins or modes depending on the version used.

## 5.2. CCAM, CTM, GLOMAP

## 6. DMS Climatology Modelling

The way in which DMS is created and enters the atmosphere needs to be considered when attempting to model its effects on climate. There are a number of ways in which this can be treated: using large data maps, modelling the ocean, and/or applying different methods for ocean surface-to-atmosphere exchange (surface flux) (Woodhouse et al., 2010). These climatological models of DMS are needed to produce the chemical concentration maps used as input for any chemical transport model (see section 5.2.2).

### 6.1 Modelling DMS production

A number of studies exist for modelling DMS. Their methods provide guidance for which modelling systems are successful, and which DMS climatological models are necessary to produce realistic results.

The Pacific Atmospheric Sulfur Experiment (PASE) measured DMS and SO<sub>2</sub> levels via flights made at 40 m above sea level in the remote Pacific Ocean, near Christmas Island (Bandy et al., 2011). Other chemicals were also measured, including H<sub>2</sub>SO<sub>4</sub>. Using this data Simpson et al. (2014) devised budgets for DMS, SO<sub>2</sub> and NSS sulphate particles. The DMS budget consisted of surface flux, entrainment, oxidation and divergence. Using the budgets it was calculated that approximately 20 % of DMS became NSS sulphate particles.

In the region measurements were taken from, an easterly jet stream from South America introduced NSS sulphate particles, originating from the land, into the MBL. This was exacerbated by a localised subsidence. Modelling showed that the particles introduced via FT entrainment dominated those produced from DMS for the region (Simpson et al., 2014). The study revealed that their results were influenced by regionally specific inputs that may not be present in the GBR, and highlights the importance of localised modelling and the potential influence of particles from the FT (Simpson et al., 2014).

## 6.2. DMS SURFACE FLUX

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Woodhouse et al. (2010) produced a global model of DMS and its effects on CCN concentration. Aerosol processes were modelled using GLOMAP-mode inside of a chemical transport model called TOMCAT. A number of DMS climatologies were tested, with the climatology developed by A. J. Kettle et al. (2000) as a reference point (see section 6.2). The model showed that DMS's highest impact on CCN was in the southern hemisphere (see figure 6.1). Also, any region with large anthropogenic CCN sources sees little impact from DMS (Woodhouse et al., 2010). Overall, the global impact of DMS on CCN in the model was low. It was also found that changes to CCN production from different climate change scenarios could not be distinguished from variances arising from using different climatology models.

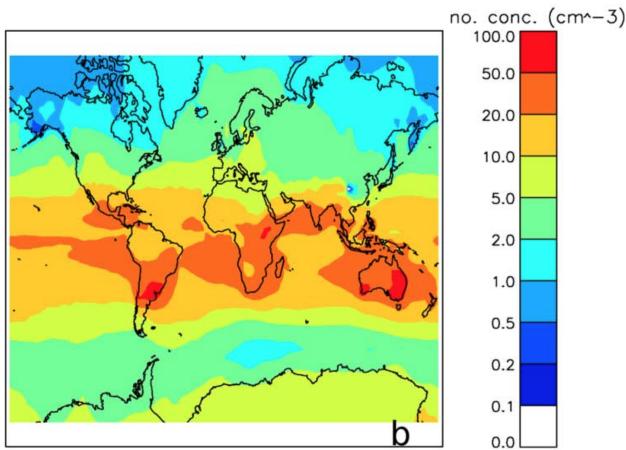


Figure 6.1: A global map of the difference between CCN concentrations produced by model runs with and without DMS (Woodhouse et al., 2010).

## 6.2 DMS Surface Flux

As mentioned in section 5.2.2, maps of the chemicals being analysed are required to feed into any chemical transport model used. For DMS, this is often given as a surface flux map for the region of interest. There are many meteorological and biological variables influencing DMS surface flux. The major meteorological variable is wind speed at the surface of the ocean (A. J. Kettle et al., 2000). Surface concentrations of DMS are generally taken from experimental data with a flux model producing atmospheric concentrations (Woodhouse et al., 2010).

A. J. Kettle et al. (2000) describes a methodology for approximating a global DMS surface flux map. Data was collected from a large number of publications, study databases and direct correspondence with researchers (see figure 6.2). The data

was then interpolated to provide monthly global  $1^{\circ}$  resolution sea surface DMS maps. Maps for sea surface salinity, temperature and chlorophyll concentration were also created (A. J. Kettle et al., 1999). In A. J. Kettle et al. (2000) the surface concentration maps from A. J. Kettle et al. (1999) were converted to surface flux maps using a technique from Liss (1983). The transfer rate was assumed to be a function of the concentration difference between the ocean and air, and the piston velocity, which depends on wind speed. Other surface flux methods were also examined and the differences between them produced an error in DMS results greater than 50 %. Overall, the method showed little dependence on meteorological changes to DMS flux, around 10 % for future predicted changes.

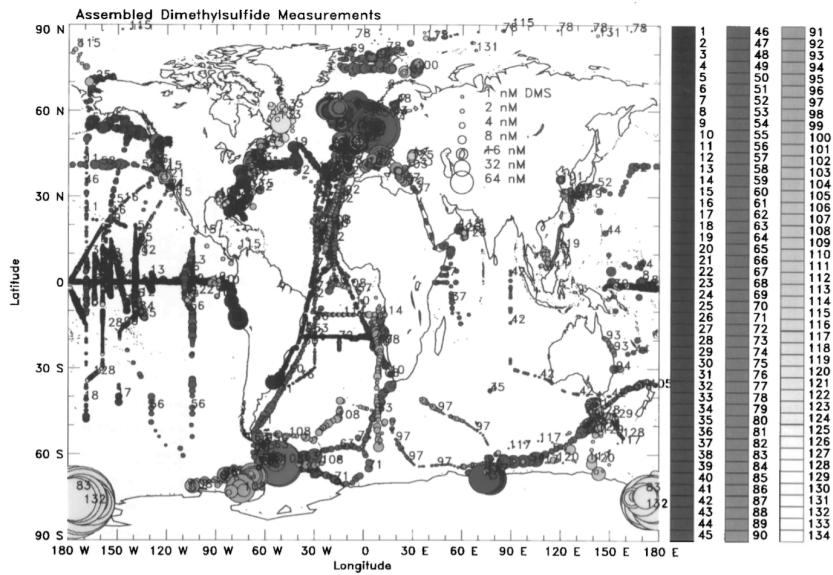


Figure 6.2: The global measurement data used for producing interpolated maps of DMS sea surface concentrations (A. J. Kettle et al., 1999). Larger circles indicate higher concentrations while shading defines the contributor.

Lana et al. (2011) expanded on this work producing a more complete and accurate climatological model of DMS surface flux. Their model indicates a summer increase in surface flux (see figure 6.3) and also a vertical dependence on atmospheric DMS concentration. The database of measurements used was also three times larger than that of A. J. Kettle et al. (1999), resulting from continued efforts into the SOLAS project (Surface Ocean Lower Atmosphere Study) (Lana et al., 2011).

The observational data for the GBR was largely sourced from G. B. Jones et al. (2005). Interestingly, both ocean surface and atmospheric DMS concentrations were measured in this study. The significance of a regional and diurnal dependence on DMS concentrations indicates that the global results obtained in Lana et al. (2011) should not be assumed for regionally specific models.

## 6.2. DMS SURFACE FLUX

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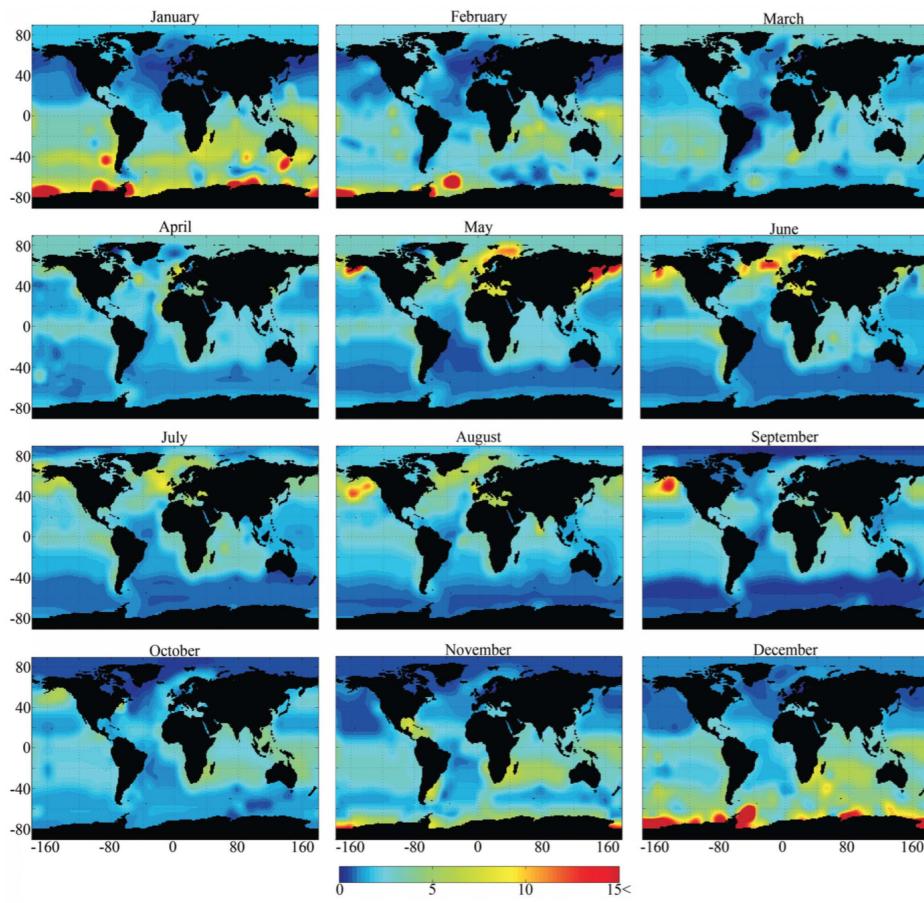


Figure 6.3: Monthly global maps of DMS concentrations produced using surface concentrations and an updated surface flux parameterisation (Lana et al., 2011). Increases in DMS concentrations during summer periods can be seen.

## **7. Summary**

### **7.1 Evaluation**

The sources included in this literature review establish the underlying science of the DMS to CCN process being analysed in this Honours project. They provide a clear image of the DMS pathways needed to create a model of this process in the GBR and northern Queensland region. The papers chosen in section 3.2 illustrate the disputed state of the CLAW hypothesis while care has been taken to understand all angles without prejudice. For chapter 5, foundational technical papers describing models were chosen to build a base understanding. Care was taken to include recent sources to ensure the current model versions are well understood. Modelling research on DMS, reviewed in chapter 6, was chosen for its relevance to the project and its impact on current literature.

### **7.2 Knowledge Gap**

As the great barrier reef is such a large structure, and ocean temperatures are increasing (Hoegh-Guldberg, 1999), the effect these changes have on coral is important. The production of DMS by coral is well established (G. B. Jones et al., 2005; Fischer et al., 2012) and changes in coral coverage will effect this production. Furthermore, results from Fischer et al. (2012) indicate that while coral production of DMSP increases in bleaching scenarios, the atmospheric DMS levels decrease drastically. Fischer et al. (2012) suggests this will decrease cloud cover due to the DMS, CCN connection, further driving bleaching. The scale of the GBR, and current bleaching levels, makes this an important relationship to explore.

Global models are well developed for the relationship between DMS production and cloud coverage, however they contain large uncertainties (Woodhouse et al., 2010). Cainey et al. (2007) indicates that this is due to regional variability and

### 7.3. CONCLUSION

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calls for regionally specific modelling. While Quinn et al. (2011) used global modelling to refute the global negative feedback loop in the CLAW hypothesis, they acknowledged that more regional modelling needs to be done to understand locally contained negative feedback loops. The satellite study performed by Leahy et al. (2013) indicated the importance of including variation from local sources when modelling, particularly in regions where coral bleaching occurs.

The analysis of current chemistry relating to DMS and its products in section 3.1 are important for considering source and sink terms for DMS within the modelling system. Ensuring that the chemical reactions are treated with respect to current theory will improve predictions. In section 3.2.2 the different ways in which DMS is prevented from eventually forming CCN was summarised. These mechanisms will need to be incorporated into the operation of both CTM and GLOMAP-mode.

DMS surface flux values are required to provide input into CTM. Changing ocean surface temperatures and wind speeds alter this flux through the mechanisms outlined in section 6.2. A surface flux model, potentially taking meteorological data from CCAM will need to be developed. It may be possible to alter the surface flux model to simulate a number of different scenarios resulting from changes in climate and changes in coral cover.

It is clear that regionally specific aerosol models are necessary for reducing uncertainties in climate modelling, and that DMS producing biota serve a role in effecting climate. The GBR is very high producer of DMS (G. B. Jones et al., 2005), with localised influences on production levels, making it an excellent candidate for regional modelling.

## 7.3 Conclusion

In this literature review the existing research surrounding DMS, and its effects on CCN production, has been examined. The focus was on modelling the system for the GBR region. Investigating the atmosphere, its many layers, and the aerosols in it established the underlying theory for CCN, and for atmospheric modelling. Reviewing the chemistry and role of DMS, and coral's production of it in the GBR, identified the requirements for modelling chemical transport and the creation of new particles. The models to be used were examined for their function and viability. Finally the climatology of DMS was researched and methods for developing maps of DMS surface flux were found. This literature review indicates that there is a necessity for localised models of the GBR's effect on cloud cover that existing research

## CHAPTER 7. SUMMARY

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has not covered. The application of the CCAM, CTM, GLOMAP-mode modelling system to the GBR will elucidate the role of coral on climate and the impacts of coral bleaching.

### 7.3. CONCLUSION

## **Part II**

# **Research**



## **8. Methodology**



## **9. Results**



## 10. Analysis



## 11. Discussion



## **12. Future Research**



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