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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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# Acknowledgements

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# Chemicals

DMS Dimethyl sulfide. 4, 13, 15, 16, 17, 18, 19, 20

DMSO Dimethyl sulfoxide. 15, 16

DMSO<sub>2</sub> Dimethyl sulfone. 15, 16

DMSP Dimethylsulfoniopropionate. 17, 18

H<sup>+</sup> Hydrogen. 16

H<sub>2</sub>O Water. 12, 16

H<sub>2</sub>SO<sub>4</sub> Sulfuric acid. 15

MSA Methane sulfonic acid. 15, 16, 18

MSIA Methane sulphinic acid. 15, 16

NO<sub>3</sub> Nitrate. 15

OH Hydroxide. 15

SO<sub>2</sub> Sulfur dioxide. 15

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> Ammonium sulphate. 14



# Abbreviations

**CCAM** The Conformal-Cubic Atmospheric Model. 4

**CCN** Cloud Condensation Nuclei. 3, 4, 9, 10, 12, 13, 15, 17, 18, 19, 20

**CLAW** The Charlson Lovelock Andreae Warren hypothesis. 4, 16, 17, 18, 19, 20, 21

**CSIRO** Commonwealth Scientific and Industrial Research Organisation. 4

**CTM** The Chemical Transport Model. 4

**FT** Free Troposphere. 7, 8, 19, 20

**GBR** Great Barrier Reef. 4

**GLOMAP** The GLObal Model of Aerosol Processes. 4, 12

**MBL** Marine Boundary Layer. 7, 11, 12, 17, 19, 20

**NSS** Non-Sea-Salt. 17, 18

**PBL** Planetary Boundary Layer. 7, 8

**RH** Relative Humidity. 8, 9

## Part I

# Literature Review



# 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.

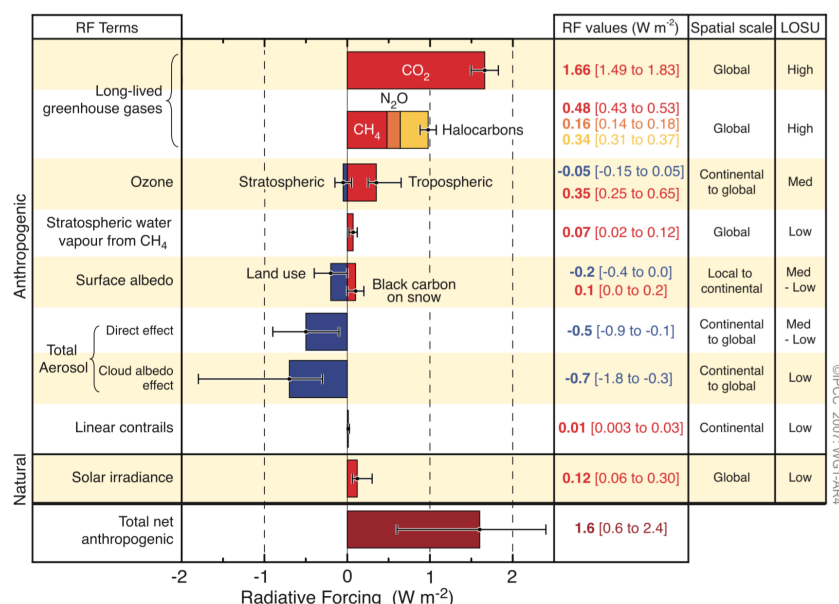


Figure 1.1: A diagram illustrating the various influences on radiative forcing along with their associated uncertainties. From the 2015 Intergovernmental Panel on Climate Change. The largest contributor to uncertainty is currently aerosols (IPCC, 2015).

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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 (Caine et al., 2007; Simpson et al., 2014).

In 1987 the CLAW hypothesis, named after the authors, was defined in the seminal paper ‘Oceanic phytoplankton, atmospheric sulphur, cloud Albedo and climate’. 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.



## 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

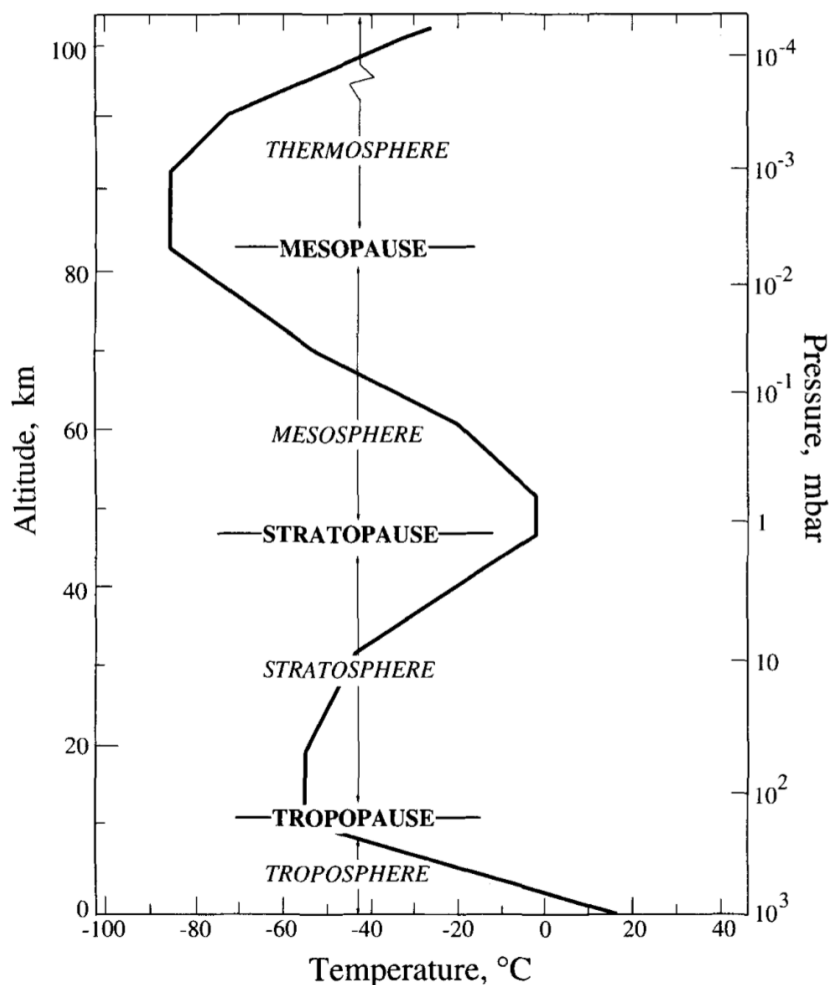


Figure 2.1: The layers of Earth's atmosphere, separated by pauses in temperature change with respect to altitude (Seinfeld et al., 2012, p. 7)

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).

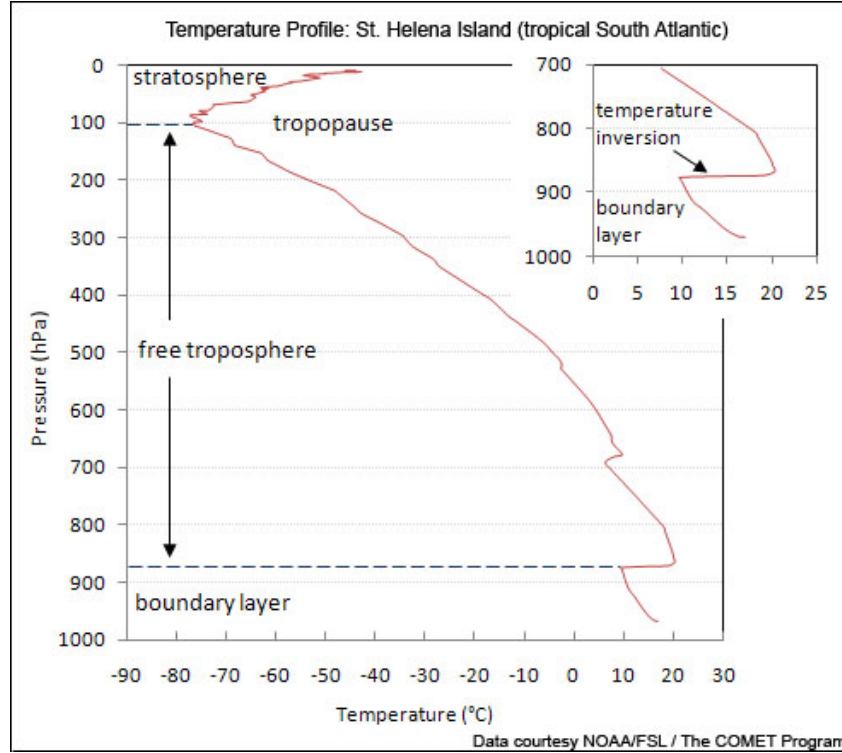


Figure 2.2: An example of the separation between PBL and FT at St. Helena Island. There is an inversion layer present distinguishing the two, however, this obvious separation is not always the case. (Laing et al., 2011, Section 1.5.1)

## 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

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).

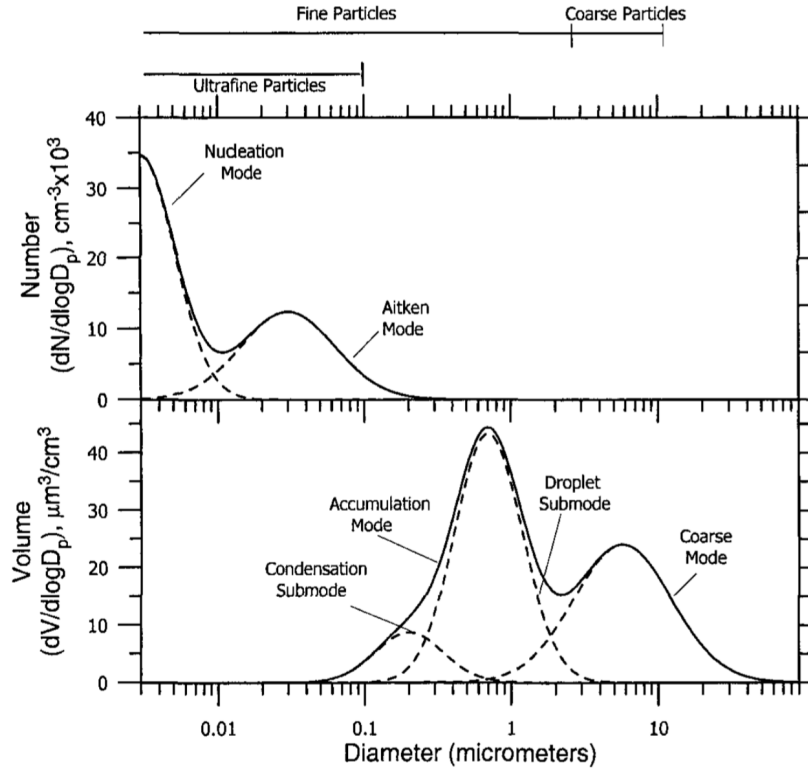


Figure 2.3: A example of the Number and Volume distributions of atmospheric particles indicating the various modes. (Seinfeld et al., 2012, Chapter 8)

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

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  $\text{H}_2\text{O}$  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  $25 - 3500 \text{ cm}^{-3}$  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

Substituting in the known constants produces  $\frac{4M_w\sigma_w}{RT\rho_w} \approx \frac{0.66}{T}$  and  $\frac{6n_sM_w}{\pi\rho_w} \approx \frac{3.44 \times 10^{13}vm_s}{M_s}$  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,

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

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  $v = 3$ ,  $M_s = 132.14 \text{ g mol}^{-1}$ .

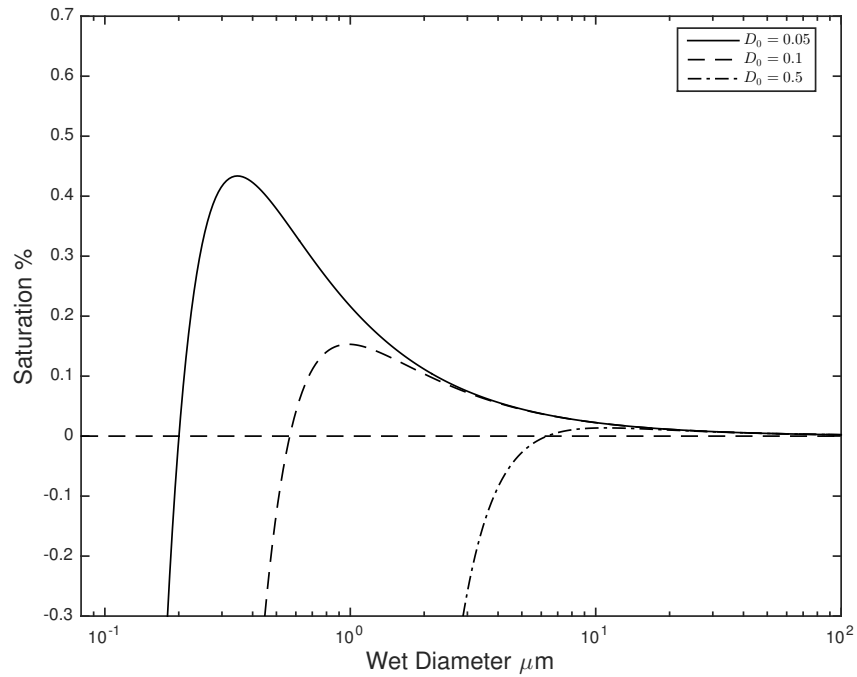


Figure 2.4: The Köhler curves for ammonium sulphate  $(\text{NH}_4)_2\text{SO}_4$  for three dry diameters 0.05, 0.1, 0.5  $\mu\text{m}$  using approximations from Seinfeld et al. (2012, p. 770)

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

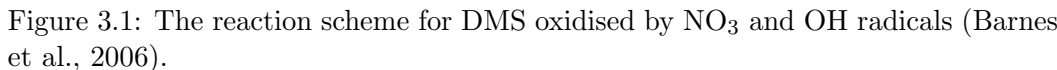
Dimethyl sulphide (DMS) is a naturally produced chemical that has been theorised to influence cloud coverage and potentially act as a negative feedback mechanism for climate change (Charlson et al., 1987). DMS enters the atmosphere and goes through an array of chemical reactions to produce sulphuric acid ( $\text{H}_2\text{SO}_4$ ) (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 3.1). 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  $\text{NO}_3$  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  $\text{NO}_3$  as seen in figure 3.1 (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.,



### 3.1.1 Multiphase Chemistry

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

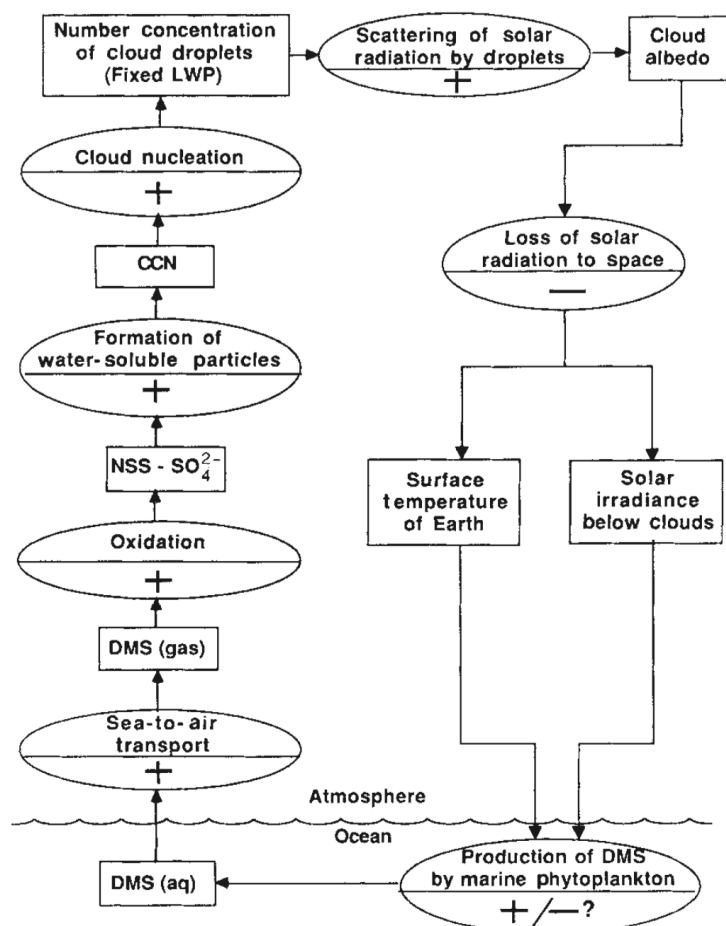


Figure 3.2: The original feedback loop diagram describing the CLAW hypothesis postulated in the paper by Charlson et al. (1987). Rectangles are measurables, ovals are processes. The sign indicates the effect a positive change in the previous rectangle has on the next rectangle. The appearance of both 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.

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 3.2, 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

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

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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).

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 3.3.

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 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 (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

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et al. (2011) argues that the majority of DMS derived particles present in the MBL are from this process.

Caine 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.

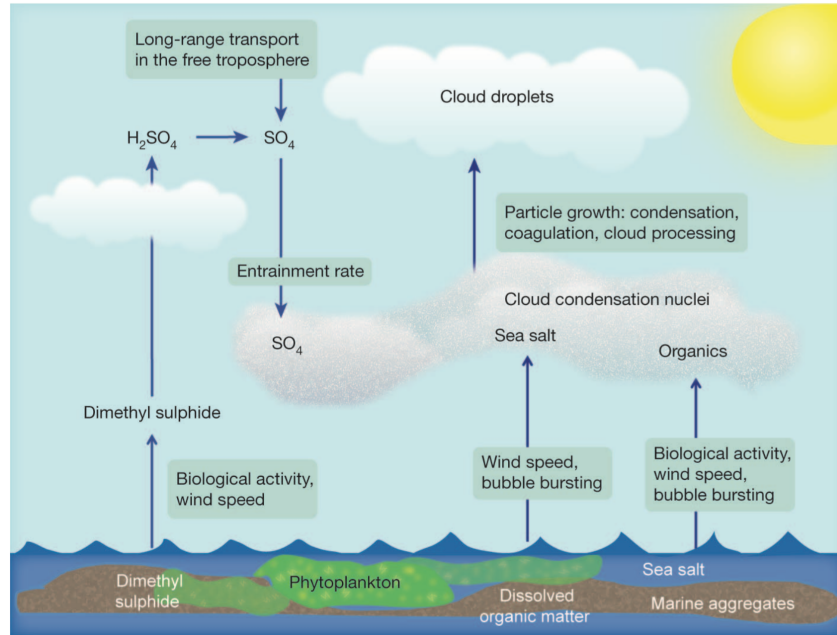


Figure 3.3: An updated cycle for CCN production in the MBL. Major changes to the cycle in figure 3.2 are nucleation in the FT driven by clouds, and the presence of sea salt and primary organic aerosols (Quinn et al., 2011).

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; Caine 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  $1.3^\circ\text{C}$  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 (Caine 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



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.



## Part II

# Research



## 4. Methodology

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## 5. Results

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## 6. Analysis

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## 7. Discussion

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## 8. Future Research

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