Quantifying the role of marine phytoplankton (DMS) in the present day climate system

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7.

SUMMARY

7.1 Summary of Results Obtained for Individual Objectives of the Study

A hypothesis of a feedback cycle through which marine phytoplankton can influence climate was proposed by Charlson *et al*. [1987]. Briefly, this hypothesis suggests that atmospheric sulphate particles of oceanic algal origin may serve as nucleation sites for water vapour and thus lead to cloud droplet formation. These cloud droplets are effective scatterers of incoming solar radiation and when in high concentrations may lead to a cooling of climate. In a feedback loop, this cooling of climate could negatively affect algal blooming (which is partly temperature-dependent) and the subsequent production of dimethylsulphide gas, the sulphate aerosol precursor.

Mainly using the hypothesis of Charlson *et al*. [1987] as a motivation and basis, this Ph.D. research has aimed to quantify the extent to which marine phytoplankton are able to influence climate through modifying the energy budget of the Earth, in order to determine whether or not this influence is significant. The specific objectives of the study have been:

1) *to quantify and analyse the climatic significance of the return of incoming solar radiation to space by coccolithophore blooms in open ocean waters.*

The water-leaving radiance, defined as radiation from the sun reflected by particles in water and exiting the ocean surface back into the atmosphere and space, is often used to derive ocean-colour information from remotely sensed data. However, it is in itself a measure of the amount of solar irradiance reflected by oceanic constituents and, therefore, not available to the Earth's heat reservoir (changes in which can affect the Earth's energy balance and climate). A strong influence on the water-leaving radiance is observed from coccolithophore blooms, owing to the highly reflective calcareous platelets or coccoliths which cover these marine algae and are also shed by them and are suspended in water. In this study, satellite remotely sensed water-leaving radiances (1998-1999) over the North Atlantic Ocean, where the blooms are spatially and temporally most abundant, were analysed. We found that the direct radiative forcing of climate between 402-565 nm (the major range of optical influence) by coccolithophores in this ocean is negligible (-0.05 W m^{-2} mean annually, Figure 1).

To put this in perspective, the global mean annual radiative forcing of highly scattering anthropogenic sulphate aerosol particles in the present day climate has been estimated at -0.4 W m^{-2}, while that combined for the greenhouse gases carbon dioxide, methane, nitrous oxide and halocarbons has been estimated at +2.43 W m^{-2} [IPCC, 2001]. The radiative forcing of the stratospheric ozone hole has been estimated at -0.15 W m^{-2} while that of tropospheric ozone has been estimated at +0.35 W m^{-2} producing a net forcing of +0.2 W m^{-2} [IPCC, 2001]. Comparatively, the mean annual solar radiation *received* at the Earth's surface ranges from 80 W m^{-2} over the Arctic to 280 W m^{-2} over the Sahara desert, where cloud cover is negligible [Strahler and Strahler, 1992].

On a local scale, however, intense backscattering of solar irradiance by coccolithophore blooms has the potential to affect local meteorological (e.g. wind patterns, evaporation, convection) and physical oceanographic processes (e.g. vertical mixing in the water column, currents, and the wind mixed layer depth), which may in turn be relevant to ecological issues (e.g. feedbacks of changes in water motion on plankton dynamics). The local radiative forcing of a large coccolithophore bloom (~5 x 10^5 km^2 in extent) in the North Atlantic was quantified using satellite data. This forcing (-2.5 W m^{-2} between

402 and 565 nm - the major range of coccolithophore optical influence) for the duration of the bloom (visible phases only) may be large enough to affect physical processes in the surface ocean and lower atmosphere in the vicinity of and during the bloom. However, microscale meteorological and oceanographic measurements in locations of coccolithophore blooms, which were beyond the scope of the current study, would be necessary to confirm these proposed linkages [Gondwe *et al*., 2001; Chapter 2].

2) *to quantify and analyse the contribution of marine algal-derived DMS to the global atmospheric burdens of DMS, MSA, SO_2, and nss $SO_4^=$.*

Some prominent phytoplankton groups produce dimethylsulphoniopropionate (DMSP), presumably for the purpose of controlling osmotic pressure and relieving photosynthetic and oxidative stress [Kirst, 1996; Stefels, 2000, Kiene *et al*., 2000, Sunda *et al*., 2002]. DMSP is released into the water when microalgal cells are ruptured during consumption by zooplankton, after cell lysis at the end of a bloom or due to viral lysis [Dacey and Wakeham, 1986; Malin *et al*., 1992; Malin and Kirst, 1997]. Dimethylsulphide (DMS) is formed as an algal or bacterial enzyme-mediated degradation product of DMSP [*e.g.* Bates *et al*., 1994; Stefels, 2000; Kiene *et al*., 2000]. Most of this DMS is subsequently consumed by bacteria or is photo-oxidised in the water at a rate depending on microbial activity and photochemical conditions [Kiene *et al*., 2000]. However, the remaining part, which forms only a small fraction of the entire in-water pool of DMS [Kiene and Bates, 1990]), is emitted to the atmosphere where it undergoes chemical transformation to eventually form methanesulphonate (MSA), sulphur dioxide (SO_2) and non sea salt (nss) sulphate aerosols ($SO_4^=$) among other sulphur products. Sulphate aerosols play an important role in the earth-atmosphere radiation balance through partial scattering, absorption and reflection of solar and terrestrial radiation. They may also serve as nucleation sites for the formation of cloud droplets which, in turn, play an important role in the Earth's climate through partial scattering, reflection and absorption of solar and terrestrial radiation.

In this thesis, use is made of a global three-dimensional chemical transport model (TM3) to quantify the atmospheric burdens of ocean-derived DMS, MSA, SO_2 and the climate-relevant nss $SO_4^=$ relative to all other sources of these chemical species. Other sources of these chemical species considered in this study are transportation emissions, industrial emissions, volcanic emissions, terrestrial DMS emissions (e.g. from oxic freshwater lakes and vegetation [e.g. Wakeham and Dacey, 1989; Hines *et al.*, 1993]) and biomass burning emissions. Analyses are made at a spatial resolution of 7.5^o x 10^o, with 19 layers in the vertical dimension extending from the Earth surface to the stratosphere. Annual mean results show that ocean-leaving DMS makes a large contribution to the total atmospheric column burdens of DMS and MSA over all oceanic areas, with global mean contributions of 98% and 94%, respectively. For SO_2 and its oxidation product nss $SO_4^=$, the contributions are greatest over the Southern Hemispheric oceans. As opposed to the Northern Hemisphere, the Southern Hemispheric industrial sulphur source is weak and, therefore, marine DMS emissions control observed SO_2 and nss $SO_4^=$ concentrations. On a global scale, the annual mean contributions are 32% and 18%, respectively (Figure 1).

Modelled data have been extensively validated against published measurements and TM3 has been found to perform reasonably well in reproducing the observed species concentrations [Gondwe *et al*., 2003; Chapter 3].

3) *to quantify and develop a global picture of the spatial and temporal distribution of the MSA: nss $SO_4^=$ ratio.*

The only known precursor of methanesulphonate aerosols (known as methane sulphonic acid in the gas phase) is DMS. As such MSA aerosols are a good tracer of DMS presence or oxidation in the atmosphere. Nss $SO_4^=$, on the other hand, also has precursors other than DMS, such as industrial SO_2 emissions, SO_2 emissions from transport vehicles (e.g. inter-continental shipping vessels), volcanic SO_2 emissions and other smaller natural or anthropogenic sulphur emissions. As such it can alone not be used to deduce the strength of the marine algal contribution to possible climate effects by the aerosol. Isotopic analyses [e.g McArdle and Liss, 1995; McArdle *et al*., 1998; Patris *et al.*, 2000] offer a means of isolating this contribution since different sulphur sources have different sulphur isotopic

composition and so the isotopic signature of marine biogenic sulphate (though currently not yet fully constrained) can be distinguished from that of an anthropogenic source.

Another approach in estimating the relative contributions of continental and marine sources to the global sulphur cycle is the use of the MSA: nss $SO_4^=$ ratio in air or precipitation (ice or snow). This ratio is a measure of the relative marine biogenic contribution to the total atmospheric sulphur burden and has long been measured in various parts of the globe. A high ratio suggests that a considerable fraction of the total nss $SO_4^=$ burden being observed is derived from the atmospheric oxidation of DMS, while a low ratio implies that the contribution of DMS to the total nss $SO_4^=$ burden being observed is low. Transect studies and observations from a network of stations have in the past provided some idea of the spatial and temporal behaviour of the ratio in various regions, but gaps in knowledge still existed in other parts of the globe. In this thesis, MSA: nss $SO_4^=$ ratios are modelled using a 3-D chemical transport model, and the results are compared to published measurements of the ratio. The global coverage of the model results facilitate understanding of the globe-wide spatial variation and distribution of the ratio, which was previously not offered by measurements alone. As in Chapter 3 (objective 2) above), analyses are made at a spatial resolution of 7.5^o x 10^o x 19 layers, but results are presented only for the lower atmosphere.

Comparison of modelled versus measured data shows fair model performance in most regions of the globe, with the exception of the Arctic atmosphere, where the MSA: nss $SO_4^=$ ratio is consistently overestimated. Our results confirm that the ratio is generally highest around the polar regions and lowest within the tropics. This is attributed to the fact that MSA is best produced under low ambient temperatures (maximum ambient temperature of 27^oC [Mauldin *et al*., 1999]).

In spite of the fact that MSA is preferably produced under low temperatures, observations at high latitudes have consistently shown summer maxima and winter minima in the MSA: nss $SO_4^=$ ratio [e.g. *Ayers et al*., 1986, 1991, 1996 at the Cape Grim measurement Station in Southern Australia and *Li and Barrie*, 1993 and *Li et al*., 1993 at Alert in Canada and Barrow in Alaska] which has puzzled many on the validity or robustness of the theory of the MSA production mechanism. As a solution to this puzzle, diminished marine biological activity and low seawater DMS conditions in winter have widely been cited as the cause of this observed trend [e.g. *Minikin et al.,* 1998; *Legrand and Pasteur,* 1998]. This study proposes that despite temperatures at high latitudes being low and therefore, favourable for MSA production, photochemical OH production during the dark winter months at polar latitudes is marginal. Consequently, reduced wintertime oxidation of DMS by the photochemically produced hydroxyl radical (OH) to form MSA, results in summer maxima and winter minima in MSA concentrations at these latitudes. Temperature and marine biological activity are, therefore, not the only major determining factors for MSA production at high latitudes on a seasonal scale. Light conditions too are important.

We estimate the Northern Hemispheric, Southern Hemispheric and global annual mean MSA: nss $SO_4^=$ ratios resulting from all sulphur sources at 0.08, 0.20, and 0.14, respectively (Figure1). The global mean annual ratio of 14% is comparable to the 13% contribution estimated for oceanic DMS emissions to the total global lower atmospheric concentrations of nss $SO_4^=$ using the tagged tracer method [Gondwe *et al.*, 2003b, Chapter 3]. This good agreement points to a high reliability of using the MSA: nss $SO_4^=$ ratio in determining the DMS contribution to observed sulphate concentrations.

Analyses of modelled MSA: nss $SO_4^=$ ratios resulting from all sources show that throughout the year, the highest ratios occur in the Southern Hemisphere, where the atmospheric DMS burden is highest (for reasons explained in Objective 2) above and in Chapter 3). This is in agreement with short- and long term atmospheric and ice core measurements of the MSA: nss $SO_4^=$ ratio from literature.

The MSA: nss $SO_4^=$ ratio resulting solely from the oceanic DMS source is consistent for the Northern Hemisphere (33%), Southern Hemisphere (33%) and on a global scale (31%), pointing to a stable model performance in the oxidation of DMS under various conditions [Gondwe *et al*., 2004; Chapter 4].

4) *to quantify the amount of energy returned to space by nss $SO_4^=$ particles of oceanic DMS origin and analyse the significance to climate.*

In this thesis a global 3-D radiative-convective model (KRCM; 10^o x 10^o x 27 layers) is used to resolve the question of how much energy is reflected back to space by algal-derived nss $SO_4^=$ aerosols and

assess whether or not this is significant. Two scenarios are examined: a *control* scenario wherein all sources of nss $SO_4^=$ minus the marine DMS source are considered and a *pertubation* scenario wherein all nss $SO_4^=$ sources considered in the control scenario plus the marine DMS source are considered. Radiative transfer calculations made for the control scenario provide information on the amount of energy that would be scattered back to space by sulphate aerosol particles if phytoplankton did not exist in the present day climate system while the pertubation scenario provides information on the amount of energy that is scattered back to space in the present day climate due to the presence and existence of marine phytoplankton.

Results show the greatest radiative pertubation to be in the Southern Hemisphere (-0.04 W m^{-2}, mean annually) where the algal derived nss $SO_4^=$ burden (and, therefore, optical depth) is also greatest. For the Northern Hemisphere and on a global scale, the pertubation is estimated at -0.02 W m^{-2} and -0.03 W m^{-2} mean annually, respectively (Figure 1). Comparatively, the global annual mean direct radiative forcing of anthropogenic sulphate aerosols is estimated to be -0.4 W m^{-2} by the Intergovernmental Panel on Climate Change [IPCC, 2001].

The negative radiative pertubation induced by marine DMS derived sulphate aerosols is mainly located above oceanic areas, close to the source, and because the albedo of the background water does not overwhelm the Earth-leaving radiance.

The trend (which is steep at low sulphate aerosol concentrations but forms a semi-plateau at high sulphate aerosol concentrations) of the relationship between scattering-aerosol concentrations and their optical depth, and the radiative pertubation calculated from them, results in a situation whereby the overall addition of DMS derived sulphate aerosol to the atmosphere generally has a less dramatic impact on the radiative balance as would be the case in a preindustrial scenario, where anthropogenic sulphur emissions are neglected. In the relatively pristine preindustrial atmosphere (*i.e.*, low scattering-aerosol concentrations), the addition of new scattering particles (oceanic DMS derived sulphate) would cause a dramatic increase in the aerosol optical depth and subsequently the radiative pertubation calculated from it (Chapter 5).

5) *to quantify the contribution of modelled algal-derived nss $SO_4^=$ particles to the global cloud droplet number concentration (CDNC).*

The column (surface to upper atmosphere) density of cloud droplets regulates the penetration of solar and terrestrial radiation through a cloud cover. Marine algae contribute to the Earth's energy balance through indirectly adding to the column cloud droplet number concentration (CDNC). We calculate mean column CDNC that may be created by marine algal-derived sulphate aerosols on global and annual scales under various atmospheric conditions according to the parameterisations of Boucher and Lohmann, [1995, relationship D] which relate sulphate aerosol mass to CDNC. Analyses are made at a resolution of 7.5^o x 10^o x 19 layers. We estimate the Northern Hemispheric, Southern Hemispheric and global annual mean column CDNC of oceanic DMS origin to be 95 cm^{-3} (34% of total CDNC), 118 cm^{-3} (77% of total CDNC), and 106 cm^{-3} (49% of total CDNC), respectively (Figure1). These contributions seem rather large in relation to the anthropogenic sulphur contribution which is approximately 5x larger than the DMS contribution at the global scale [Gondwe *et al.*, 2003, Chapter 3]. The reason for this is that the Boucher and Lohmann parameterisation, tends to overestimates CDNC at low sulphate mass concentrations relative to other proposed methods.

Generally, the highest CDNC of oceanic DMS origin occurs above the Southern Hemispheric oceans where low industrial sulphur emissions, relative to the Northern Hemisphere, do not overwhelm the sulphate aerosol burden. In particular, the highest CDNC occurs above the tropical southeastern Pacific Ocean where, ironically, the lowest satellite-observed chlorophyll *a* concentrations (*i.e.,* marine algal abundance) in the global ocean occur. Several published measurement campaigns in the southeastern Pacific atmosphere show that CCN (cloud condensation nuclei) accumulation due to repeated processing of aerosols through several non-precipitating cloud cycles are a dominant occurrence in this region, where atmospheric subsidence is dominant and suppresses precipitation. Once a cloud evaporates without precipitating, the CCN are released to form part of the available aerosol population. The released aerosols are larger and active at low supersaturation. When the conditions are met, they readily nucleate new cloud droplets, increasing the CDNC.

These observations are further supported by our analyses of the Legates/MSU rainfall climatology and International Satellite Cloud Climatology Project (ISCCP) data which show that the southeastern

Pacific region has a high cloud amount, but a relatively low cloud optical depth (τ_c between 5 and 10) and low rainfall. The same is true for the southeastern region of the tropical South Atlantic Ocean and oceanic region off the Australian west coast, where we have also identified a high oceanic algal derived CDNC.

ISCCP data also show that the cloud droplets in these regions have large effective radii. Analyses of the relationship between cloud droplet effective radius and cloud albedo using global multiyear ISCCP data by Han *et al.*, [1998a] show that cloud albedo increases with increasing cloud droplet radii for all optically thin clouds (τ_c <15), implying a considerable climatic effect of the high marine algal derived CDNC estimated for these regions.

The spatial location of maxima in the CDNC resulting from all sulphur sources also has interesting, but different implications. Hotspots of CDNC resulting from all sulphur sources are found above continental regions, especially above the highly industrialised regions of the eastern United States, eastern Europe and China. Han *et al.* [2000] analysed ISCCP data and found that for most optically

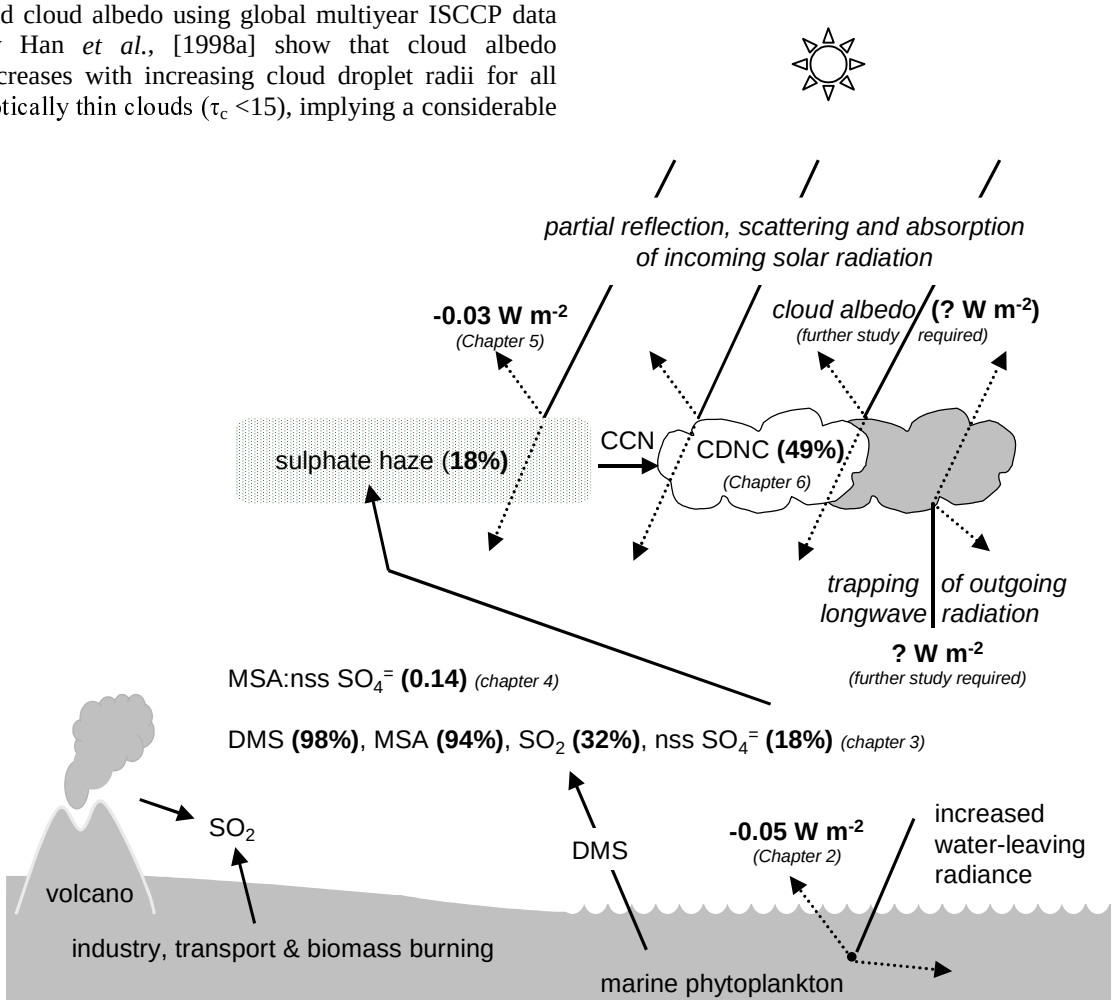

Figure 1: Some of the pathways of influence of marine phytoplankton on climate. The quantities shown have been determined in the research presented in this thesis and represent the marine algal contribution to the concentrations, burdens and radiative pertubation. All quantities presented are global annual means, with the exception of the results of Chapter 2, which are valid for only the North Atlantic Ocean. Results for Chapters 3 and 6 are valid for a troposphere-stratosphere column, while those for Chapters 4 and 5 are valid for the troposphere. To put the quantities in perspective, the mean annual shortwave radiation absorption by the Earth-atmosphere system = 235 W m^{-2} [Harrison *et al.*, 1990].

thin (τ<15) continental clouds, as is the case in the hotspot regions, there is little albedo change due to changes in the column cloud droplet number concentration, but that for similar clouds above the oceans, the albedo response is large. The reason for this is that the column cloud droplet number concentration in continental regions is higher than that in marine regions where CCN sources are fewer and smaller lower. This observation by Han *et al.* [2000] suggests that in a hypothetical world without marine phytoplankton, the absent contribution of DMS to the CDNC would not make a big difference to the albedo of optically thin continental clouds and probably currently does not.

Furthermore, the impact of clouds over land on the net radiation budget is usually less than over the adjacent ocean regions since there is less cloudiness. Where there are clouds, the forcing usually still remains low (relative to the adjacent ocean) since the contrast in albedo between the clouds and the underlying bright ground surface is low [Harrison *et al.*, 1990] (Chapter 6).

7.2 Remarks

Although the global DMS emission is approximately one-fifth of the global anthropogenic sulphur emission [see Chapter 3, "Data and Methodology section"], DMS does not necessarily contribute one-fifth of the total sulphate-induced radiative pertubation of climate. The contribution is much less. The reason for this is the non-linearity of the Earth's climate system. For instance, the very high global anthropogenic sulphate aerosol burden results in a situation where the addition of DMS-derived sulphate aerosols to the atmosphere, increases the sulphate aerosol optical depth (*i.e.*, in a linear relationship), but does not make a huge impact to the total sulphate aerosol-induced radiative pertubation. This is so since aerosol optical depth and its related radiative pertubation are not linearly related and their relationship has a trend which is steep at low sulphate aerosol concentrations but forms a semi-plateau at high sulphate aerosol concentrations (see Chapter 5). This implies that under a future warmer climate, a possible increase in oceanic DMS-derived sulphate aerosols, would also not make a huge impact on the sulphate aerosol-induced radiative pertubation as near-saturation in the global sulphate aerosol optical depth seems to already have been reached today.

Similarly, the trend of the relationship between CDNC and cloud albedo is steep at low sulphate concentrations but is plateau-like at high sulphate aerosol concentrations. As such the addition of marine DMS-derived cloud droplets to the existing CDNC in a future climate, would also most likely not result in a significant cloud albedo increase.

While the global effects quantified in each individual chapter may be low relative to those caused by other climate forcing agents (such as atmospheric CO_2 concentrations), together they might form a considerable amplified effect on a regional scale, where the effects are much higher, with consequences on local climate.

It is important to note that although multiyear satellite-deduced mean annual distribution of chlorophyll *a* (a proxy for phytoplankton presence and abundance) in surface oceanic waters (Figure 2a) shows great concentration of these algae at mid- to high latitudes in the Northern Hemisphere, a global mapping of seawater DMS concentrations measured between 1972 and 1999 has shown that the hemispheric mean annual seawater DMS concentrations are almost comparable in magnitude (1.4 nM L^{-1} in the Northern Hemisphere versus 1.7 nM L^{-1} in the Southern Hemisphere) [Kettle *et al.*, 1999]. The global emissions inventories of Bates *et al.* [1992] and Anderson *et al.* [2001] correspondingly show an even distribution of natural sulphur emissions between the Northern and Southern Hemisphere[1].

This discrepancy between the location of high chlorophyll *a* concentrations and that of high surface seawater DMS concentrations and emissions is attributed to the fact that different phytoplankton species have different chlorophyll *a* concentrations and that not all phytoplankton species are strong DMSP producers [Turner *et al.*, 1989; Keller *et al.*, 1989; Keller and Korjeff-Bellows, 1996; Corn *et al.*, 1996]. As such DMSP production per unit chlorophyll is not a 1:1 relationship and varies from species to species, with members of the classes Dinophyceae and Prymnesiophyceae producing copious amounts of DMSP; members of the classes Bacillariophyceae (diatoms) and Prasinophyceae producing intermediate amounts; and members of the classes Chlorophyceae,

[1]An exception is the Simó and Dachs [2002] empirically-derived database which shows that the mean surface seawater concentration of DMS in the Southern Hemisphere is approximately half that in the Northern Hemisphere.

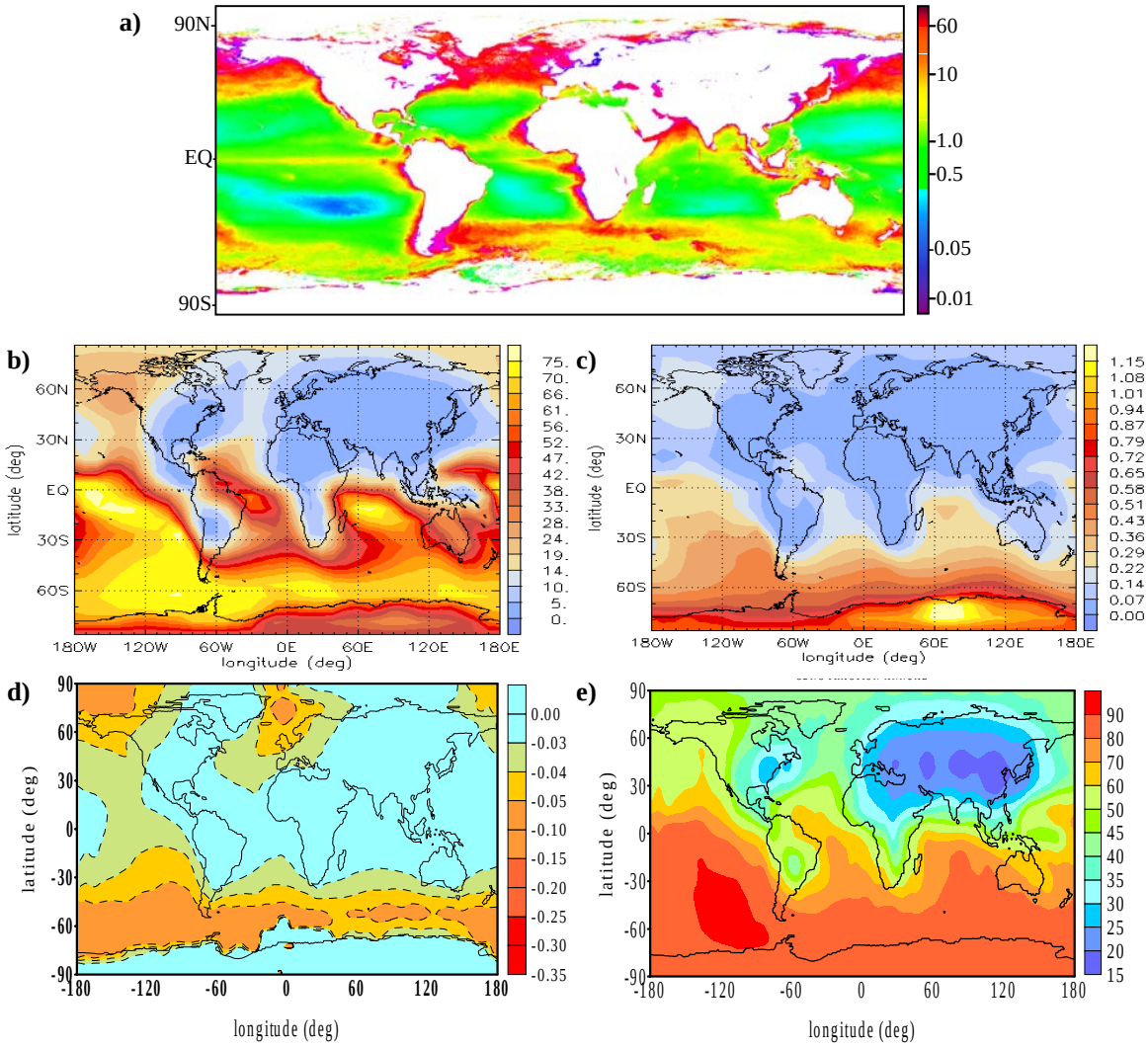

Figure 2: Although satellite-deduced (SeaWiFS) mean annual distribution of chlorophyll *a* (mg m^{-3}), a proxy for phytoplankton presence in surface oceanic waters **(a)** shows great concentration of these algae at mid- to high latitudes in the Northern Hemisphere, the mean annual measured seawater DMS concentrations [Kettle *et al.*, 1999] in the Northern and Southern Hemispheres are of comparable magnitude (1.4 nM L^{-1} and 1.7 nM L^{-1}, respectively). Furthermore, despite the comparable magnitude of seawater DMS concentrations in the two hemispheres, the greatest climatic impacts of marine DMS are found to occur at mid- to high latitudes in the Southern Hemisphere (*this study*): **(b)** = the percentage of the annually averaged nss $SO_4^=$ column burden attributable to ocean-leaving DMS alone (TM3 model, *this study - Chapter 3*); **(c)** = the mean annual surface (~1009 hPa/ 35m) MSA: nss $SO_4^=$ ratio as modelled by the TM3 model (*this study - Chapter 4*). The predicted ratios are >1 in some areas due to the additional input of MSA from overlying and neighbouring model layers. Runs were conducted for a total of 19 vertically-stacked layers extending from the ground surface up to the stratosphere; **(d)** = the mean annual energy (W m^{-2}) lost to space through sulphate particles of marine DMS origin (KRCM model results, *this study - Chapter 5*); **(e)** = the mean annual percentage of cloud droplet number concentration (cm^{-3}) indirectly originating from ocean-leaving DMS (using Boucher and Lohmann [1995, relationship D], *this study - Chapter 6*).

Cryptophyceae and Cyanophyceae producing the least amounts of DMSP [Corn *et al.*, 1996; Keller and Korjeff-Bellows, 1996]. In addition to the variable abundance and spatial dominance of other moderately DMSP-producing algae such as diatoms, the Southern Ocean in the Southern Hemisphere is also one of the preferred niches for *Phaeocystis* (Prymnesiophyte) [Keller *et al.*, 1989; Smith and Dunbar, 1998; Bates *et al.*,1998; DiTullio *et al.*, 2000] and coccolithophores (Prymnesiophyte) [Brown and Yoder, 1994]. These algae have high intracellular DMSP per unit chlorophyll [Liss *et al.*, 1994; Keller and Korjeff-Bellows, 1996].

Furthermore, despite the fact that satellite-deduced mean annual distribution of phytoplankton in surface oceanic waters (Figure 2a) shows great concentration of these algae at mid- to high latitudes in the Northern Hemisphere, the greatest climatic impacts of marine DMS have been found to occur at similar latitudes, but in the opposite (southern) hemisphere (*this study*, Figures 2b-e). In the Southern Hemisphere, it is the high sea-to-air flux of gases (especially in the mid- to high latitudes) compared to the Northern Hemisphere [e.g. Burgermeister *et al.*, 1990; Huebert *et al.*, 1993; Simó and Dachs, 2002] that partly leads to an elevated annual mean DMS column burden in the atmosphere. A reduced oxidative capacity of the Southern Hemispheric atmosphere relative to that of the Northern Hemisphere further leads to the accumulation of DMS in the Southern Hemispheric atmosphere and an elevation in its atmospheric burden. Furthermore, the Southern Hemisphere has a larger sea surface area from which DMS is emitted compared to the Northern Hemisphere and this also heightens the atmospheric DMS burden in the Southern Hemispheric atmosphere. The large surface roughness presented by the presence of large land masses in the Northern Hemisphere also supports meridional mixing of DMS and its oxidation products in the atmosphere, with a consequent reduction in the atmospheric column burdens of the chemical species at mid- to high latitudes. Comparatively, the surface area of land masses in the Southern Hemisphere is smaller and mainly confined to the low latitudes. Reduced surface roughness at mid latitudes allows circumpolar flow to prevail. Meridional mixing is, therefore, limited and atmospheric chemical constituents above the southern ocean accumulate when removal processes are weak. The overall consequence of an elevated atmospheric DMS burden in the Southern Hemispheric atmosphere is that the climate-relevant product of atmospheric DMS oxidation (namely, nss $SO_4^{=}$) and its' climate impacts are also concentrated in the Southern Hemisphere.

It is, therefore, clear that a global rather than case study was necessary for the topic of this thesis since non-linearities in the ocean-climate system can lead to unexpected variations in the expected spatial trends of processes. The selection of a study area and sampling locations in multidisciplinary studies should, therefore, be made prudently as important regions in one field (e.g. seawater DMS dynamics) may not be important in another (e.g. DMS-related cloud microphysics).

Continued spatially and temporally comprehensive measurements remain necessary to improve the Kettle *et al.*, [1999] database. This, together with continued efforts in improving DMS sea-air flux determination will allow better assessment of the magnitude of the flux of oceanic DMS to the atmosphere. This will, in turn, enable fine-tuning of the strength of the DMS-climate relationships determined in this study. Furthermore, continued tuning and validation of model parameterisations remains vital in lending credibility to the results of models on DMS-climate relationships.

7.3 Feedbacks

Field measurements [e.g. Ayers *et al.*, 1991; Bates and Quinn, 1997] and modelling studies alike [e.g. this thesis] have since the late 1980s provided bits of evidence for the climatic significance of DMS emissions. Parallel to this, evidence has also been sought for the hypothesised feedback link whereby climate affects the level of DMS emissions.

Charlson *et al.* [1987] hypothesised that algal blooms may become more abundant under a possible warm future climate, with the consequence that DMS production may increase. Regional atmospheric pressure and, therefore, wind patterns and precipitation are also expected to change in a future warm climate [e.g. IPCC, 2001]. Some areas of the globe, such as the Southern Hemispheric mid-and high latitudes are expected to experience increased wind speeds [e.g. Gillett and Thompson, 2003]. Considering that current sea-to-air fluxes deplete only a small fraction of the entire in-water pool of DMS [Kiene and Bates, 1990; Bates *et al.*, 1994], such an increase in wind speeds over marine areas imply a greater potential for increased DMS emissions in the future through

increased sea to air gas transfer [Wanninkhof and McGillis, 1999].

Bates and Quinn [1997] conducted multi-year shipboard measurements (1982-1996) in the Equatorial Pacific Ocean, a region where the El Niño Southern Oscillation (ENSO) phenomenon is triggered. Due to the ENSO, large interannual variations occur in oceanic sea surface temperatures, mixed layer depths, and upwelling rates with matching responses in atmospheric temperatures, pressure, circulation patterns and precipitation. This area is, therefore, an ideal location for observing variable atmospheric conditions, some of which are consistent with expected atmospheric conditions in a warm future climate. Results from this study, however, show that despite large ENSO-induced oceanic and atmospheric variations, total biomass and the mean surface seawater DMS concentration in this region remains relatively constant both seasonally and interannually. Analysis of the impact of ENSO-driven changes on the sea-to-air flux of DMS was, however, not made by these authors.

In the atmosphere, the situation observed on an interannual scale is different. Sciare *et al*. [2000] conducted long-term (1990-1999) continuous measurements of atmospheric DMS at Amsterdam Island in the southern Indian Ocean. Both positive and negative anomalies (*i.e*. the difference between a given mean and its historical mean) were observed on a monthly scale. Further analysis using a combination of modelling and observations showed that this variability could not be explained by meteorology or the oxidative capacity of the atmosphere, but rather by changes in the DMS source strength.

Empirical analyses by Simó and Pedrós-Alió [1999] and Simó and Dachs [2002] support the likelihood of a negative feedback of climate on seawater DMS concentrations. Using a combination of satellite remotely sensed data, climatological geophysical data and modelling, these authors found a negative correlation between DMS and mixed layer depth in >80% of the global ocean surface. Increased wind stress in a future climate would increase oceanic mixed layer depth which would in turn lead to lower DMS concentrations. Using a global 3-D ocean carbon cycle model, Aumont *et al*. [2002] similarly investigated the effect of changing mixed layer depth (as would occur in a warmer future climate) on phytoplankton growth rate. These authors found reduced primary production with increasing mixed layer depth. Using a coupled ocean-atmosphere general circulation model in conjunction with a biogeochemical model and satellite remotely-sensed data Belviso *et al*. [2000] correspondingly found a global decrease (~5%) in sea surface DMS concentrations under a warm future climate.

Gabric *et al*. [1998] used an atmospheric general circulation model and a DMS production model to investigate changes in the sea-to-air flux of DMS under doubled CO_2 concentrations in the atmosphere (*i.e*. a future climate that is 4^{o}C warmer than the present one). These authors predicted a 2-8% increase in the flux of DMS to the atmosphere, with a positive effect on the CCN abundance and associated radiative effects. Similarly, Sciare *et al*. [2000] predicted a strong positive influence of SSTs on atmospheric DMS concentrations, also in agreement with the *in situ* observations of Sciare *et al*. [1999].

Using a simple model based on empirical relationships Foley *et al*. [1991] predicted a minor influence of climate changes on DMS production and flux, and cloud albedo.

As can be seen, the sign of the feedback of climate changes on DMS emissions is found to be variable, being either positive or negative under different circumstances. This might suggest that feedbacks of opposite signs in a warm future climate will probably compensate one another leading to a small net feedback effect.

It is, furthermore, important to draw attention to the fact that an assessment of the present day climate by the IPCC [2001] has noted an increase in global lower atmospheric temperatures of 0.15^{o}C per decade since 1979. This warming has induced an extensive retreat of glaciers and sea-ice in the northern hemispheric mid- and high latitudes. However, no such warming or sea ice-retreat has been observed over the Southern hemispheric oceans and Antarctica. This suggests a slower response of the Southern Hemispheric oceans to atmospheric warming, with consequent slower or lower changes in phytoplankton dynamics, DMS(P) production, and feedback effects in this region.

7.4 Recommendations for Future Research

Although the impact of marine phytoplankton on climate (e.g. this thesis) and vice versa (e.g the feedback studies discussed above) have widely been investigated, some issues still remain to be researched. For instance, the change in albedo induced by cloud

droplets of oceanic DMS, as well as the amount of outgoing longwave radiation sent back to Earth by these droplets, still need to be quantified (see Figure 1) for an even more comprehensive quantitative understanding of the role of marine phytoplankton on climate. Due to nonlinearities and feedbacks in cloud microphysics, such studies would require the use of detailed cloud microphysical models.

7.5 References

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