Coccolithophore-derived production of dimethyl sulphide

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INTRODUCTION

It is hard to find a research paper or book on coccolithophores that does not include a few sentences on the role of this fascinating and enigmatic marine phytoplankton group in the production of dimethyl sulphide ($(CH_3)_2S$; DMS). Our aim here is to provide some general background information on DMS for non-specialists, but also to highlight current knowledge and what we believe to be significant gaps, for those with a specific interest in coccolithophores, other haptophytes and DMS.

Lovelock et al. (1972) first discovered that DMS was ubiquitous in the sea and suggested that sea-to-air emission of this compound was a key pathway in the global sulphur cycle. Marine DMS emissions are thought to account for about 23% of the sulphur entering the global atmosphere but, because anthropogenic sulphur tends to deposit rapidly and close to source, the biogenic flux contributes 42% of the final atmospheric column burden (Chin and Jacob, 1996). Hence DMS inputs to the atmosphere are of greatest significance in areas that are distant from anthropogenic sulphur sources (Bates et al., 1987; Savoie and Prospero, 1989; Twomey, 1991). Once in the air DMS oxidises quite rapidly mainly via hydroxyl radicals during the day, nitrate radicals at night (the latter being more significant in polluted areas), and reactions with halogen oxides may also be significant (Ballesteros et al., 2002; Plane, 1989; Ravishankara et al., 1997). DMS oxidation leads to the formation of a number of sulphur compounds including sulphur dioxide, sulphate, methanesulphonic acid (CH_3SO_3H; MSA), dimethylsulphoxide ($(CH_3)_2SO$; DMSO) and dimethylsulphone ($(CH_3)_2SO_2$; $DMSO_2$).

In the 1980's and early 1990's research largely focussed on the contribution of natural DMS emissions to the global sulphur budget, and the wet and dry deposition of the acidic atmospheric oxidation products of DMS (natural 'acid rain'). However, there was a substantial shift in emphasis after Charlson et al. (1987) picked up on the earlier suggestion of Shaw (1983) and put forward the hypothesis that sulphate aerosols derived from marine DMS emissions influenced cloud albedo and global climate. A simple depiction is shown in **Fig. 1**. Sulphur aerosol influences climate in 2

ways: directly since aerosol particles scatter incoming radiation reflecting some of it back into space, and indirectly because the aerosols produced are of the ideal size and chemistry to act as cloud condensation nuclei, and these influence cloud albedo and cloud formation, again reflecting radiation from the Sun and so cooling the Earth. The so-called CLAW hypothesis (named after the initials of the authors Charlson et al., 1987) was controversial in that they suggested that the DMS–cloud albedo system would operate under negative feedback such that a climate change would be countered by an opposing change in DMS production. A great deal of debate ensued particularly regarding the climatic role of natural versus man-made aerosols derived from anthropogenic SO_2 emissions. Nonetheless, CLAW has provided great impetus for all aspects of research on DMS.

DMS is a biogenic trace gas derived from the cellular precursor dimethylsulphoniopropionate ($(CH_3)_2S^+CH_2CH_2COO^-$; DMSP), a zwitterionic compound that is found in the cells of certain types of marine phytoplankton and seaweeds. Both DMS and DMSP are essentially ubiquitous in the marine euphotic zone, although concentrations show considerable spatial and temporal variation. In recent years increasing attention has been paid to the biogeochemical, physiological and ecological roles played by DMSP and DMS. The haptophyte algae appear to be key players in global DMS production, and data obtained from blooms and cultures of *Phaeocystis* and the coccolithophore *Emiliania huxleyi* constitute a vital part of our current understanding of DMS/DMSP production, transformation and cycling.

DMSP – THE MAJOR PRECURSOR OF DMS

DMSP is considered a structural analogue of glycine betaine ($(CH_3)_3N^+CH_2COO^-$) a quaternary amine compound that is well known as a compatible solute in many higher plants (Sakamoto and Murata, 2002). Such organic compounds are accumulated so that plants can acclimate to environmental stresses such as changes in salinity and low temperature. DMSP has been shown to have some of the typical properties of a compatible solute (Kirst, 1996). However, recent exciting research on trophic interactions {(Steinke et al., 2002c; Wolfe et al., 1997) phytoplankton physiology (Stefels, 2000) and the novel proposal that DMSP counters oxidative stress (Sunda et al., 2002), all suggest that DMSP functions way beyond its basic role as a compatible solute.

DMSP PRODUCTION BY HAPTOPHYTES

The seminal laboratory studies of Keller and co-workers give an excellent overview of cellular DMSP levels in 127 marine phytoplankton cultures covering representatives of 12 different algal classes (Keller, 1989; Keller et al., 1989a; Keller et al., 1989b). The clonal cultures used were grown in nutrient rich media and analysed for total DMS plus DMSP content during the logarithmic phase of growth. From these studies a general ‘rule of thumb’ emerged that has been a guiding influence for many subsequent laboratory and field studies, i.e. that haptophytes and some

dinoflagellates have higher intracellular levels of DMSP than diatoms. In Table 1 we review the Keller et al. data for haptophytes. The list of coccolithophores covers *E. huxleyi* and 5 other clones, all of which accumulated high intracellular concentrations of DMSP. Of the non-coccolith bearing haptophytes high intracellular DMSP levels were found in a range of species including *Chrysochromulina* spp.*, Isochrysis galbana, Pavlova* spp.*, Phaeocystis* spp. *and Prymnesium parvum.* Where data is available for several clones of one species considerable variation in DMSP levels can sometimes be observed. Whilst there is no doubt that the Keller et al. data is still a valuable resource, exceptions to the general rule mentioned above have emerged notabley the high concentrations of DMSP in some ice diatoms (e.g. Bouillon et al., 2002; Kirst et al., 1991; Levasseur et al., 1994) and in planktonic diatoms under conditions of oxidative stress (Sunda et al., 2002) . The considerable recent advances in the understanding of haptophyte phylogeny and ecology, and the increased availability of clonal cultures (see chapters by van Lenning et al., Probert et al. in this volume) would permit a far more comprehensive survey of DMSP in haptophytes today.

In addition to taxonomy, factors including low temperature, nitrogen and light availability may also influence the DMSP concentration observed in marine phytoplankton cells. Compatible solutes typically increase in concentration when the growth temperature is decreased and this is true for DMSP for some polar seaweeds (Karsten et al., 1996; Karsten et al., 1992) and the prasinophyte *Tetraselmis subcordiformis* (Sheets and Rhodes, 1996). Three pathways for DMSP synthesis have been elucidated (see Stefels, 2000), but for a range of marine algae including *E. huxleyi* synthesis appears to be initiated by transamination of methionine. The pathway then proceeds via reduction and methylation reactions to a novel intermediate 4-dimethylsulphonio-2-hydroxybutyrate (DMSHB) and this is converted to DMSP via oxidative decarboxylation (Gage et al., 1997). The transamination step releases a valuable NH_3^+ group for general cell metabolism which fits with suggestions that DMSP would be preferentially synthesised under nitrogen limitation. In agreement with data in the early DMSP literature Keller and Korjeff-Bellows (1996) found that cellular DMSP increased with nitrogen limitation in a few marine phytoplankton, but a subsequent detailed investigation found no clear inverse relationship between cellular levels of glycine betaine and DMSP relative to nitrogen availability (Keller et al., 1999a; Keller et al., 1999b). Stefels (2000) suggested that DMSP synthesis could function as a metabolic overflow mechanism for excess reduced compounds and energy when growth is unbalanced e.g. due to nitrogen limitation. This would enable photosynthesis, methionine synthesis and other essential metabolic processes to continue. Cellular production of DMSP utilises methionine, keeping its level low to prevent possible inhibitory feedbacks and releases N for essential metabolic processes.

Studies on DMSP and DMS production versus light intensity have produced rather mixed results. Vetter and Sharp (1993) found that *Skeletonema costatum* produced 50% less DMS at 38 µmol m^-

^{2} s^{-1} than at 380 µmol m^{-2} s^{-1}. The difference was more pronounced during senescence, but under low light the DMS production rate per cell matched or exceeded that of the high light culture during its extended log phase. In contrast the apparent release of DMS by *Phaeocystis antarctica* was minimal at 350 µmol m^{-1} s^{-1} and 26.6 fg DMS per pg cell carbon at 3.5 µmol m^{-2} s^{-1}, but there was no overall relationship between light intensity and DMS output (Baumann et al., 1994). Keller and Korjeff-Bellows (1996) found no significant or consistent common response to light intensity in terms of DMSP content in 4 microalgae including *E. huxleyi*. However, Arctic clones of *Phaeocystis* sp. were found to have higher rates of DMS production at low irradiance (Matrai et al., 1995) and Stefels et al. (1996) found that DMSP production continued in the dark period of a light/dark cycle in a temperate *Phaeocystis* clone. These data suggest that DMSP production is not directly linked to light and that the light history and overall cellular physiological state are the critical factors. Very few studies have considered the combined effects of nutrient and light stress. An excellent exception is the study of Stefels and van Leeuwe (1998) who examined whether the overall effects of iron limitation in an Antarctic *Phaeocystis* clone, were due to reduced energy supply because of reduced photosynthetic activity or nitrogen insufficiency. They found that DMSP concentration increased under high light, iron-deficient conditions when *Phaeocystis* cells were close to nitrogen-deficiency, but did not decrease under low light and iron limitation when the cells were more severely energy limited. Cell volumes were reduced significantly under low iron, but this reduction in volume was only accompanied by a reduction in DMSP content when light levels were low. At high light intensity cellular DMSP concentrations increased.

Recently, Sunda et al. (2002) put forward an exciting and intriguing hypothesis that DMSP, DMS, acrylate, dimethylsulphoxide ($(CH_3)_2SO$; DMSO) and methane sulfinic acid (CH_3SO_2H; MSNA) and their related breakdown products constitute an antioxidant system in marine microalgae that may be regulated via DMSP lyase activity (DLA). All living cells have mechanisms to deal with reactive oxygen species (ROS) such as superoxide $O_2^{-\bullet}$, H_2O_2, singlet oxygen and the $^{\bullet}OH$ radical. Oxidative stress occurs when a cell's capacity to prevent or repair ROS damage is exceeded. Environmental factors, e.g. osmotic stress, low temperature nutrient limitation high light, high or low temperature and chemical toxicity can increase ROS production levels. As already discussed some of these conditions are known to increase DMSP concentration in phytoplankton cells. In support of their hypothesis Sunda et al. (2002) demonstrated that in both *Thalassiosira pseudonana* (low constitutive DMSP) and *Emiliania huxleyi* (high DMSP) increased UV radiation, increased Cu^{2+}, CO_2 limitation and iron deficiency all increased cellular DMSP levels. The level to which marine phytoplankton depend upon this antioxidant system rather than well-established antioxidants such as glutathione or ascorbate is not yet known. In 2 separate field studies the 0.7 - 10µm size fraction DMSP (Belviso et al., 1993) and DLA (Steinke et al., 2002b) were found to covary with the concentration of photoprotective pigments. These data are complementary to the

proposed hypothesis though no direct links between photoprotective pigment levels and oxidative stress were made.

STUDIES IN COCCOLITHOPHORE BLOOMS

From the field perspective, blooms of *E. huxleyi* are well known as areas of high DMS production and have provided an excellent model system for studying DMS production in a field situation. *E. huxleyi* is unusual amongst the coccolithophores in that it sheds its ornate calcium carbonate coccoliths, and given that these are small and numerous (approx. coccosphere diameter 5 µm, coccolith diameter 2.5 µm, coccolith weight 1.8 pg, 23-30 coccoliths per cell) they accumulate and scatter light, thereby affecting the optical properties of the surface ocean (Brown and Yoder, 1994). Such blooms can cover very large areas of the ocean and some stunning satellite images can be found in the literature and on various web sites (see chapters by Tyrell and Balch this volume). There has sometimes been a tendency to assume that the white water blooms seen via satellite are always dominated by *E. huxleyi.* However, in our experience of studies where detailed phytoplankton identification and enumeration has been carried out, this has been relatively rare. Indeed several field studies give strong indications that coccolithophores other than *E. huxleyi,* particularly *Calcidiscus leptoporus*, *Gephyrocapsa, Coccolithus pelagicus* and *Crystallolithus* (the motile holococcolith-bearing phase of *C. pelagicus)* may also be important DMS producers (Holligan et al., 1993; Holligan et al., 1987; Malin et al., 1993; Savidge and Williams, 2001; Turner et al., 1988). In other *E. huxleyi* bloom studies nanoflagellates and/or dinoflagellates have contributed a significant portion of the particulate DMSP (DMSPp) observed (Archer et al., 2002b; Steinke et al., 2002a).

The ability to find and track white waters by accessing satellite images whilst onboard ship has been exploited during several DMS-focussed field campaigns (e.g. Holligan et al., 1993; Malin et al., 1993; Matrai and Keller, 1993). The most recent of these have been Lagrangian studies where the volatile tracer sulphur hexafluoride (SF_6) has been used to label and then track the movement and dispersal of an *E. huxleyi* population (Burkill et al., 2002; Jickells, 2002; Read and Pollard, 2001). The principal use of the SF_6 tracer technique has been in studies designed to test the validity of parameterisations used to estimate air-sea fluxes of volatile compounds (Nightingale et al., 2000; Watson et al., 1991b), but following the suggestion of Watson et al. (1991a) the SF_6 mapping technique has been used to label open ocean areas with and without the simultaneous addition of nutrients. This powerful tool has led to significant advances in physical and biological oceanography e.g. during iron fertilisation experiments (Boyd and Law, 2001; Martin et al., 1994). Of particular note here are a 3.5 fold increase in DMS concentration following iron addition in the Pacific (Turner et al., 1996b), increases in prymnesiophyte DMSP followed by grazing-induced DMS production after iron fertilisation in the Southern Ocean (Boyd et al., 2000), a 4.7 fold increase in DMS over 9 days in a northeast Atlantic cold-core eddy that most likely resulted from

production associated with *C. pelagicus* (Savidge and Williams, 2001), and studies which considered the production and turnover of DMSP and DMS in *E. huxleyi* blooms in the North East Atlantic and the northern North Sea which show the dominant influence of heterotrophic processes on the quantity of DMS available for sea-to-air exchange (e.g. Archer et al., 2002b; Savidge and Williams, 2001; Simó and Pedrós-Alio, 1999; Steinke et al., 2002a; Zubkov et al., 2002).

STUDIES IN *PHAEOCYSTIS* BLOOMS

Amongst the non-calcified haptophytes, *Phaeocystis* blooms have frequently been noted as hot spots for DMSP production and DMS emissions (see Liss 1994). In late spring and early summer the phytoplankton population of the temperate southern North Sea is usually dominated by *Phaeocystis* and this influences water phase DMS concentrations and flux to the atmosphere in this region (Turner et al., 1996a; van den Berg et al., 1996). There has also been considerable focus on Antarctic blooms of *Phaeocystis* (e.g. Crocker et al., 1995; DiTullio, 1996; Gibson et al., 1990; Turner et al., 1995). Turner et al. (1995) compiled the published Antarctic data, derived a likely seasonal cycle for DMS and used this to estimate an annual emission of DMS to the atmosphere. There may be some bias towards coastal values in the data set, but the analysis indicated that Berresheim's (1987) earlier 86 x 10^9 mol value (~17% of the marine biogenic flux estimate of Bates et al., 1992) was rather low. Hence the influence of the Southern Ocean on the sulphur cycle is probably disproportionately greater than its 5.6% of the global ocean area would suggest. On the basis of a study in the Barents Sea, Matrai and Vernet (1997) suggested that the role of the Arctic Ocean may be similarly underestimated. Studies on Arctic *Phaeocystis* clones (Matrai et al., 1995) are supportive of this underestimation. However, Bouillon et al. (2002) found high primary production but low DMS production in the polynas of northern Baffin Bay, and the Leck and Persson (1996) estimate of 4 Gmol yr^{-1} for the total DMS flux from the northern high latitudes is less than 1% of the global estimate (Bates et al., 1992). Modelling studies suggest that the effects of global warming will be particularly enhanced in the Arctic regions and large decreases in sea ice thickness and extent have already occurred (Manabe et al., 1992; Vinnikov et al., 1999). Overall the northern polar seas have received less attention and further studies are warranted to improve understanding of DMS emissions in this region.

BEYOND PHYTOPLANKTON BLOOMS

A majority of studies on marine phytoplankton have focussed on non-equilibrium, resource-driven situations such as spring and summer blooms in temperate and polar regions, and nutrient fertilisation experiments. About 75% of all aquatic primary production occurs in the open oceans (Pauly and Christensen, 1995), where lower chlorophyll levels remain fairly uniform over wide space scales for long periods of time and picoplankton (<0.2 - 2 μm diameter) are dominant in terms of primary production and biomass. Despite DMS emissions accounting for most of the non-sea-salt sulphate and MSA in the atmosphere over remote ocean areas (Savoie and Prospero,

1989), and that it is in these regions distant from anthropogenic impact that DMS is likely to have the most influence on global climate (Charlson et al., 1987), these vast areas are relatively poorly studied in terms of DMSP and DMS production processes. Open ocean region DMS data mainly stem from studies carried out during research cruise transects which pass relatively quickly through different hydrographic zones. Such field campaigns are excellent for determining how DMS concentration varies over wide spatial scales and determining fluxes to the atmosphere. The database assembled by Kettle et al. (1999) is the most comprehensive compilation of DMS data. It contains 15,617 DMS values and has some coverage of open ocean areas. However, far smaller subsets of the data have associated DMSP or chlorophyll data, and the spatial coverage of these is poor, especially in the open ocean regions. It is clear that very few in-depth process type studies focussing on DMS and DMSP production have been done in the open ocean to date.

Somewhat contrary to other major phytoplankton groups, coccolithophore diversity is highest in warm low-productivity waters (Winter and Seisser, 1994), although the traditional view of coccolithophores as indicators of such regions has been challenged by recent studies in polar regions (Winter et al., 1999). At a very simplistic level the coccolithophore record in marine sediments gives an indication of species that were once present in the euphotic zone. The modern coccolith and carbonate flux sediment trap data of Sprengel et al. (this volume) emphasises strikingly 2 points that are relevant here. Firstly, that the cosmopolitan *E. huxleyi* is widely distributed and numerically dominant in sediments within and beyond the well-known white water areas. Secondly, other coccolithophore species are numerically important at stations in the Arctic and equatorial Atlantic, and much larger species (e.g. *Coccolithis pelagicus* and *Calcidiscus leptoporus*) dominate the carbonate export to the deep ocean throughout the Atlantic. Haidar and Thierstein (2001) examined living coccolithophore dynamics over 3 years near the BATS site in the oligotrophic North Atlantic gyre (Sargasso Sea). They found considerable seasonal and interannual variablility. *E. huxleyi* dominated throughout the year in the upper 200 metres with maximum cell densities of ~93,000 cells l^{-1}. *Florisphaera profunda* showed cell densities up to 68,000 cells l^{-1} at 100-150 m depth. The highest densities of *Umbellosphaera tenuis*, 5000 cells l^{-1}, were seen between 25-75 m, and *U. irregularis* occurred at a maximum concentration of 5000 cells l^{-1} in the upper 50 m. It is instructive to consider what such cell densities might mean in terms of field DMSP concentrations. *Umbilicosphaera sibogae* has 13.8 pg DMSP per cell (see Table 1), so if we guess at a 10 pg DMSP per cell for *U. irregularis* 5000 cells l^{-1} might contribute 0.37 nmol l^{-1} to the total DMSPp concentration. The mean *E. huxleyi* concentration of 13,000 cells l^{-1} at ~1 pg per cell (Table 1) would add an additional 0.1 nmol l^{-1}. The sum of these values lies towards the lower end of the range of DMSPp values reported by Dacey et al. (1998) for the same site, but at the very least this guesstimate underlines the idea that the larger coccolithophores could make a significant contribution to the marine DMSP pool that can be equivalent to or larger than that of *E. huxleyi*.

Many coccolithophores are known to have different life cycle stages (Billard, 1994), but most studies have concentrated on the non-motile, diploid heterococcolith stage (made up of calcified elements of different sizes and shape) where the cell is covered in its highly characteristic placoliths. During the alternate haploid phase, the cells have crystalloliths or holococcoliths (having a single type of calcified element). Special efforts have to be made to quantify and identify coccolithophores. Bollmann et al. (2002) review and compare the methods commonly that have been used, and make recommendations regarding their application and limitations. Briefly, the Utermöhl (1958) settling method is in common use for routine quantification of phytoplankton assemblages, but generally a maximum volume of 100 ml is used which can be inadequate for species which occur at low concentration. Preservatives buffered at alkaline pH are essential to ensure that coccoliths do not dissolve and the method appears to consistently underestimate cell densities. Filtration methods are often preferred in studies that focus on coccolithophores and where only coccolithophores are counted, though uneven distribution of cells on the filters can be a major problem. However, much larger seawater samples e.g. 4 to 10 l can be used and these are desiccated and counted via polarising microscopy. Where confirmation of identification is needed the same filters can also be examined using scanning electron microscopy. *E. huxleyi* and some haptophytes including *Phaeocystis* also have a motile naked cell stage. Such small flagellates are at the limits of light microscopy and generally impossible to distinguish from other picoplankton, and so analytical flow cytometry is often used for estimating numbers. The taxonomic composition of the picoeukaryote flora of the open ocean has been addressed in recent studies using molecular techniques and novel lineages, including previously unknown haptophytes, have been identified (Moon-van der Staay et al., 2001; Moon-van der Staay et al., 2000).

Detailed speciation and quantification data of the type described above has seldom been available during DMS-related field studies. Indeed, we are not aware of any studies that have included molecular analysis of phytoplankton speciation. Corn et al. (1996) found that a small range of picoplankton cultures had low but variable cellular DMSP levels with prymnesiophytes and prasinophytes showing the highest values. They applied an average DMSP per cell value to cell count data and obtained 0.7 to 2 µm fraction DMSP concentration data for a small set of oligotrophic Mediterranean samples. They concluded that the picoplankton groups contributed 10-35% of the DMSP in this small size fraction, but <1% of the total DMSP. Quantification of specific pigments is being used increasingly to quantify the contribution of different taxonomic groups within mixed phytoplankton assemblages. The pigment 19'-hexanoyloxyfucoxanthin (HEX or HFx) is considered to be diagnostic for haptophytes and has shown reasonable to good correlation with DMSP in several studies suggesting that haptophyte algae are key species for DMSP and DMS production. Belviso et al. (2001) examined pigment and DMSPp data for 200 samples from contrasting regions and concluded that the summed concentration of HEX and 19'-

butanoyloxyfucoxanthin were a reasonable surrogate for DMSPp in the <10 μm nanoplankton fraction. However, using pigment data for quantitative purposes can be problematic given that pigment composition can shift in response to a cells light history and physiological status. Furthermore, van Lenning et al. (this volume) have found that some major haptophyte families do not synthesise HEX suggesting that a single pigment comparisons may be insufficient.

To conclude this section, the combined evidence suggests that haptophytes, including the coccolithophores, are likely to be key species for DMS and DMSP production in the open ocean. Very few direct in-depth process studies have been done, and the major evidence derives from simultaneous quantification of sulphur compounds and pigments, rather than the application of detailed identification and enumeration techniques. In the future the availability of suitable hierarchical molecular probes might allow us to better address the role of the uncultured haptophyte picoplankton in the flux of biogenic sulphur from the open ocean.

DMS RELEASE FROM DMSP

Although it is clear that DMSP is the key prerequisite for DMS production in marine waters, the pathway between cellular DMSP and a pool of DMS available for emission to the atmosphere is not straightforward. To summarise briefly, a complex web of processes is involved including phytoplankton growth, exudation, autolysis, grazer activity, viral lysis, bacterial consumption and transformation of DMSP, DMS and DMSO, the activity of algal DMSP lyase, photochemical production of DMSO and sedimentation. The total marine pool of DMSP is substantial, but only a very small proportion of it is ever emitted in the form of DMS to the atmosphere, the rest being recycled within the marine food web or sedimented to deeper waters. Many diagrams visualising the biogeochemical cycle of DMS are available in the literature - excellent detailed examples can be found in the recent reviews by Simó (2001) and Kiene (2000). For the purposes of the chapter we include a simple figure that summarises current understanding of the main factors affecting the production and biogeochemical cycling of DMS. (**Fig. 2**). Even though the amount of DMS emitted to the atmosphere is a small percentage of the total potential pool, the surface of the ocean is always supersaturated with DMS relative to its atmospheric concentration which ensures a continual flux to the air. The magnitude of the flux depends on the water phase DMS concentration and the transfer velocity, a parameter, which alters the rate of gas transfer relative to wind speed, wave action, bubbles and surfactants. The physical sea-to-air gas exchange process will not be covered in any further detail here. The reader is referred to an excellent recent book on gas transfer at water surfaces (Donelan et al., 2002) and previous publications that discuss estimating DMS fluxes to the air (Malin, 1996; Turner et al., 1996a).

PROCESSES THAT INFLUENCE THE PRODUCTION OF DMS FROM HAPTOPHYTE DMSP

Phytoplankton cell lysis Little DMS is produced in exponential phase cultures of DMSP-containing phytoplankton (e.g. Stefels and van Boekel, 1993). However, cells that are compromised in some way or lyse, release their DMSP and any intracellular DMS into the surrounding environment. Recent studies suggest that cell death or autolysis of marine phytoplankton cells may be more common than was previously assumed (e.g. Agusti and Duarte, 2000; Brussaard et al., 1995), but its significance in DMS and DMSP release has not been quantified directly. The major pathways for the release of DMSP from phytoplankton cells appear to be grazing and viral lysis.

Grazing

Phytoplankton growth is always accompanied by grazing and it is not unusual for a large percentage of the marine phytoplankton to be grazed on a daily basis. Grazing can impact on the DMS cycle via incorporation of DMSP into biomass, by releasing DMSP to the water column during the feeding or digestion process and/or cleaving some or all of the DMSP to DMS prior to release. The quantity of cellular DMSP released and whether it is released as DMS or dissolved DMSP (DMSPd) has important consequences for DMS fluxes. Laboratory studies suggested that copepods and microzooplankton would influence DMS biogeochemistry (e.g. Dacey and Wakeham, 1986; Wolfe and Steinke, 1996), and further experimental evidence showed that microzooplankton-induced DMS production was related to the activity of the algal enzyme DMSP lyase (see below). However, until quite recently there was little firm evidence to demonstrate that grazing impacts on DMS production in the field.

The method most commonly used for estimating microzooplankton grazing rates is the dilution technique of Landry and Hassett (1982; Landry et al., 1995). This method was adapted by Archer et al. (2001; in press) who combined the usual measurements of net phytoplankton growth rate, with analysis of DMSPp, DMSPd and DMS concentration, bacterial abundance and net growth rate. In addition bacterial consumption of DMS was estimated in parallel incubations using the inhibitor dimethyl disulphide (Wolfe and Kiene, 1993). In 3 experiments with temperate seawater it was estimated that 14, 15 and 9% of the ambient DMSPp was converted to DMS+DMSPd by grazing (Archer et al., 2001). In a further study, estimates of the *Phaeocystis globosa* DMSPp ingested by microzooplankton accounted for the DMS production rates observed (Archer et al., in press). It was noted that extreme care had to be taken so that the filtration steps needed for setting up the dilution series did not perturb DMS and DMSPd levels. In a parallel study Wolfe et al. (2000) concluded that rapid microbial consumption and artifactual release of DMS and DMSP during filtration compromised this approach for samples from the Labrador Sea. However, a multidisciplinary Lagrangian study in a developing phytoplankton bloom in the northern North Sea

met with more positive results. High DMSPp production rates and similar DMSPp loss rates were observed suggesting high turnover. Microzooplankton grazing accounted for an average of 91% of the DMSPp lost and most of the ingested DMSPp was released as DMSPd rather than DMS (Archer et al., 2002b).

The evidence to date suggests that microzooplankton grazing is a major route for the release of DMSPp to seawater, but the modification of the dilution technique does not separate changes in DMS due to grazing from DMS production and loss due e.g. to bacterial activity and viral lysis. A selective technique for direct quantification of grazing-mediated DMS production would allow a more straightforward approach to understanding what controls DMS concentration in the sea.

Viral lysis High concentrations of viruses are ubiquitous in seawater and a significant fraction of these infect marine phytoplankton including *E. huxleyi* and *Phaeocystis pouchetii*. Malin et al. (1994; 1992) first suggested that viral lysis of marine phytoplankton cells could be an important route for the release of DMSP and DMS to seawater. Subsequently, viruses specific to suitable DMSP-containing hosts became available (Jacobsen et al., 1996), and allowed us to test this hypothesis in the laboratory. Infection of a Norwegian strain of *P. pouchetii* led to 4 fold increase in DMS concentrations over control culture levels 20 hours after virus addition, with an increase to 8 fold after 45 hours (Malin et al., 1998). In a parallel study Hill et al. (1998) observed DMS production when a non-axenic culture of *Micromonas pusilla* lysed following viral infection, but no DMS release when axenic cultures were used. The simplest explanation for this would be that *M. pusilla* has no DLA, but nothing is yet known of DLA in this strain. Molecular analysis of *E.* huxleyi-specific viruses (*Eh*V) isolated from a Norwegian fjord mesocosm and the Plymouth, U.K. coast shows that they have large double stranded DNA genomes ~410 kb in size. Phylogenetic analysis based on their DNA polymerase genes places *Eh*V in the new Coccolithovirus genus within the *Phycodnaviridae* family of algal viruses (Schroeder et al., 2002; Wilson et al., 2002b). Current work in our laboratory is examining viral lysis and DMS production using the *E. huxleyi*-*Eh*V couple with the aim of defining any link between DMS production and DLA (Evans, unpublished). However, all the virus isolates available so far infect only low-lyase activity strains of *E. huxleyi*.

With currently available techniques, quantifying the relative contribution to DMS production of viral lysis versus grazing in the natural environment remains a tough challenge. However, a promising modified dilution protocol for estimating viral mortality of phytoplankton has recently been developed (Evans et al., in press). In an *E. huxleyi* mesocosm bloom study in 2000 we observed maximum DMS concentrations after a substantial increase in the numbers of the large viruses that typically infect phytoplankton cells (quantified by analytical flow cytometry) and a concomitant collapse in the *E. huxleyi* population, which suggested a link between viral lysis and DMS production (Darroch et al. in preparation). However, in an open seawater *E.* huxleyi bloom

Lagrangian study in the northern North Sea, Wilson et al. (2002a) found no link between the numbers of large viruses and DMS or DMSP production, and it was concluded that microzooplankton grazing out-competed viral infection. Further research is necessary to determine how viruses impact the biogeochemical DMS cycle in the natural environment.

DMSP lyase activity The major pathway for the production of DMS from DMSP is thought to be via the action of an enzyme known as DMSP lyase (dimethylpropiothetin dethiomethylase, enzyme classification number 4.4.1.3) which cleaves DMSP to yield DMS, acrylate (CH_2CHCOO^-) and a proton. Several isozymes have been characterised and enzyme activity is strain specific and spans a wide range. DLA has been found in some marine phytoplankton, a marine fungus, a heterotrophic dinoflagellate and some seaweeds (see Steinke et al., 1996). However, despite DMSP lyase being a key enzyme in the biogeochemical cycle of DMS detailed information is rather limited, and the relative importance of bacterial and phytoplankton lyase enzymes is unclear. Amongst the haptophytes most attention has been paid to clones of *E. huxleyi* and *Phaeocystis*. In a *Phaeocystis globosa* isolate from the North Sea the rate of production of DMS from DMSP added directly to cultures was highest in young exponentially growing cultures and declined with culture age (Stefels and van Boekel, 1993). Further studies using crude extracts revealed the extracellular location of the enzyme and its association with the membrane fraction (Stefels and Dijkhuizen, 1996), and in the field *in vitro* assays for DLA data correlate strongly with *Phaeocystis* numbers (Stefels et al., 1995). In *E. huxleyi* DMSP lyase is located inside the cell and seems to be separated from DMSP, such that DMS production occurs when cellular integrity is compromised, e.g. when grazed by microzooplankton (Steinke et al., 1998; Wolfe and Steinke, 1996) or infected and lysed by viruses (Malin et al., 1998). Wolfe et al. (1997) demonstrated that when offered a choice of prey the heterotrophic dinoflagellate *Oxyrrhis marina,* avoided grazing on strains of *E. huxleyi* with high constitutive levels of DLA. Acrylate has antibacterial properties at high concentration, so it was proposed that *E. huxleyi* uses DMSP as the basis of a grazing-activated defence mechanism, whereby the acrylate produced during grazing deters microzooplankton from eating high-lyase strains when other food sources are available. It is also thought that the volatile product DMS could function as a signalling compound in trophic interactions. A full discussion of the role of climate relevant volatiles and related compounds in trophic interactions can be found in a review by Steinke et al. (2002c).

Two field studies in *E. huxleyi* blooms have investigated *in vitro* DLA. In the North Atlantic (Steinke et al., 2002a) activity was associated with particles >10 µm and correlated with the dinoflagellate pigment peridinin. In the northern North Sea profiles of DLA, dimethylsulphoxide (DMSO) and photoprotective pigments were coincident (Steinke et al., 2002b). It was suggested that DMSP lyase enzymes could be affected by light and that the data was supportive of the recent Sunda et

al. (2002) hypothesis which suggests that DMSP and its cleavage products are involved in scavenging reactive oxygen species.

Little is known of DLA in other haptophyte phytoplankton, but interestingly preliminary data from a recent study suggest that neither *Gephyrocapsa oceanica* (National Institute for Environmental Studies, Japan clone NIES-353) or *Isochrysis galbana* (CCMP 1324) have any significant intracellular or extracellular DLA (Niki et al., 2000).

Bacterial DMSP lyase enzymes present a problem when quantifying algal DLA in mixed assemblages. A field study by Scarratt et al. (2000) approached the question of the contribution of free and particle attached or associated bacteria to DLA, by analysing filter fractionated seawater samples. They found that DLA was associated with the larger phytoplankton-containing size fractions, and particle associated bacteria had apparent half-saturation constants for DMSP and DMS that were ~10 times that of the free-living fraction. Assuming that DMS and DMSP concentrations are enriched in the phycosphere, this suggests that different bacterial communities have the ability to utilise these compounds at a level that reflects the concentration in their immediate microenvironment

Overall understanding of the biochemistry, physiology and ecology of DMSP lyase is incomplete and requires further research. In particular a simple and reliable assay for phytoplankton *in vivo* DLA is needed to enable more realistic quantification of DMS production via this pathway in natural assemblages where intracellular and extracellular membrane-associated enzymes may be present. Steinke et al. (2000) published a small data set for such a technique which shows some potential. For clonal axenic cultures of *E. huxleyi* CCMP373 and 379 they found that *in vivo* rates of DLA were 2.8 and 5 times lower than *in vitro* values, and differences of a similar order were found with 3 samples from the North Sea (1.7, 2.6 and 2.9 times lower). Possible problems that were noted included handling and concentrating the phytoplankton biomass so as to cause minimal cell perturbation, the choice of buffer pH and temperature for the assay and sample storage. A good database for *in vivo* DLA would enable a much better appraisal of the ecophysiological role of this important algal enzyme.

OTHER KEY COMPOUNDS IN THE DMS BIOGEOCHEMICAL CYCLE

Acrylic acid Despite the possible roles of acrylate (CH_2CHCOO^-; the form of acrylic acid dominant at seawater pH) as a grazing deterrent and intracellular antioxidant, few studies have focussed directly on this compound. In Antarctic coastal waters during blooms 0.001 – 1.21 μmol l^{-1} concentrations have been found (Gibson et al., 1996; Yang et al., 1994; Yang et al., 1992), but the major barrier to more in-depth studies has been the difficulty associated with the analysis of this

highly soluble compound at the nanomolar concentrations that are likely in less productive waters. However, a direct seawater injection HPLC technique under development in our laboratory, is showing considerable promise and should allow us to learn much more about the role of this 'forgotten' compound in the biogeochemical DMS cycle (Kadner, unpublished data). There has been a tendency in DMS related research to 'forget' that acrylate may derive from other potential metabolic routes and not solely and directly from DMSP cleavage. These are:

- Demethiolation of the product of DMSP demethylation 3-methylmercaptopropionate (MMPA; $CH_3S^+CH_2CH_2COO^-$) which yields acrylate and methanethiol (CH_3SH).
- Breakdown of 3-mercaptopropionate (MPA; $HS^+CH_2CH_2COO^-$) in a reaction which might also yield H_2S (see Kiene et al., 2000; Taylor, 1993).
- Via reaction of the quarternary ammonium analogue of DMSP β-alanine betaine ($CH_3N^+CH_2CH_2COO^-$) with OH^- (King, 1988).

In an Adriatic Sea study Slezak et al. (1994) investigated whether acrylic acid might influence bacterial incorporation of leucine as well as thymidine. They found some growth inhbition in 20 minute incubation experiments with acrylic acid concentrations of 1 mmol l^{-1} or more, and in 24 to 110 h experiments activity was reduced when the concentration was >10 µmol l^{-1}. They concluded that the growth of bacteria would rarely be inhibited by acrylic acid at concentrations equivalent to the nanomolar seawater concentrations of DMS, but suggested that its role in cell aggregates should be investigated. In a study on *Phaeocystis* cultures Noordkamp et al. (1998) found the concentration of acrylate in the medium increased from 0.1-1.0 µM during exponential growth to 1 to 4 µM in stationary phase. Most of the acrylate was located in the colony mucus and they suggested that microscale concentrations up to ~1 to 6 mM could exist. Although such acrylate levels could have antibacterial activity, healthy *Phaeocystis* colonies are enclosed by a strong, semi-permeable skin, which is thought to act as a physical barrier to bacteria, grazers and viruses (Hamm et al., 1999). Nevertheless, when colonies begin to decay the acrylate is likely to be readily released and therefore available for consumption by the acrylate-utilising bacteria that are common in *Phaeocystis* blooms (Noordkamp et al., 2000)

DMSO The current evidence suggests that dimethyl sulphoxide (DMSO) in seawater derives from abiotic photooxidation of DMS (Brimblecombe and Shooter, 1986; Brugger et al., 1998; Hatton, 2002; Kieber et al., 1996; Shooter and Brimblecombe, 1989) and the release of particulate DMSO from phytoplankton cells (Lee and de Mora, 1999a; Lee et al., 2001; Simó et al., 1998; Simó et al., 2000). Bacterial oxidation of DMS is also possible, but this has yet to be proven for natural seawater samples. Wet deposition of DMSO formed by atmospheric oxidation of DMS may provide an additional source to the water column. The principle loss mechanisms for marine DMSO could be via abiotic or biotic oxidation to downstream products (e.g. dimethyl sulphone) or bacterial transformation/utilisation. DMSO has been the subject of increasing attention in recent years due to the development of more sensitive and selective analytical methods (reviewed by

Simó, 1998), but despite its ubiquity in marine waters, DMSO is still a rather poorly understood component of the marine sulphur cycle (reviewed by Lee and de Mora, 1999b). It is recognised that DMS oxidation and DMSO reduction may be important in controlling sea surface concentrations of DMS and hence, the quantity of DMS available for sea to air gas exchange. Nevertheless, the major outstanding questions are whether, or under what circumstances, DMSO acts as a source or a sink for marine DMS.

BACTERIAL ACTIVITY INFLUENCES THE SIZE OF THE DMS POOL IN SEAWATER

Marine phytoplankton invest up to 15-20% of cell carbon in DMSP (Matrai and Keller, 1994; Matrai et al., 1995) and DMSP can account for 50-100% of the particulate sulphur in some species (Matrai and Keller, 1994). The total amount of carbon and sulphur sequestered in DMSP and DMS means that these compounds influence the global carbon cycle as well as the sulphur cycle. It is also worth emphasising that every molecule of DMS emitted to the atmosphere takes along 2 carbon atoms for each sulphur atom. DMSP supports 1-13% of the bacterial carbon demand in surface seawater, they can also retain it for use as an osmosolute, and it also appears that DMSP can be a major sulphur source for marine bacteria being more energetically favourable than sulphate (Kiene et al., 2000).

Given the focus of this chapter it is inappropriate to review the large body of literature on the utilisation of DMS and related compounds by cultures of aerobic and anaerobic bacteria, natural bacterioplankton assemblages and sediment slurries (see reviews by Taylor, 1993; Taylor and Visscher, 1996). Rather we will concentrate on a few recent studies that have advanced this area significantly. Kiene and Linn (2000) pioneered the use of tracer quantities of ^{35}S-DMS and ^{35}S-DMSP to quantify the turnover and fate of these compounds in seawater. They found that in coastal waters about 40% of the DMSP sulphur is rapidly incorporated into particulates and a further 40% into a dissolved non-volatile fraction (including sulphate), whereas in oceanic waters the values were 6-25% and 68-75% respectively. At lower ambient temperatures and higher DMSP concentrations volatile products dominated over particulate products, suggesting that bacterial sulphur demand was saturated. In all cases the volatile fraction was dominated by methanethiol (CH_3SH) and was consumed within 1 to 3 hours, whereas DMS was the minor product and turned over more slowly. Methanethiol readily complexes with metals and dissolved organic matter which retards its flux to the air. Radiotracer experiments show that the methiol group of methanethiol is efficiently incorporated into methionine, suggesting that it is a key intermediate in the pathway leading to incorporation of DMSP-sulphur into bacterial protein (Kiene et al., 1999).

DMSP and DMS are valuable substrates for marine heterotrophic bacteria, and bacterial uptake, consumption or transformation processes limit the emission of climatically active DMS to the atmosphere. The DMSP demethylation/demethiolation pathway appears to be the dominant sink for DMSP and DMS is usually a minor product. On the basis of culture and seawater studies Kiene et al. (2000) put forward the hypothesis that DMSP 'availabilty' controls DMS production, whereby as DMSP concentration increases the fraction of the DMSP pool converted to DMS increases until the demethylation pathway is saturated and at this point the amount of DMS produced begins to increase. This hypothesis does not necessarily require high absolute concentrations of DMSPd, since the level of bacterial sulphur demand relative to DMSP availability is the key. It is also important to note that bacterioplankton growth in the sea can be limited by nutrient availability, UV light, bacteriophage and grazing. Indeed, Simó and Pedrós-Alió (1999) proposed a relationship between mixed-layer depth (MLD) and the DMS yield from DMSP, whereby UV-B radiation reduces bacterial activity when the MLD is shallow. Additionally, studies by Zubkov et al. (2001; 2002) and Gonzalez et al. (1999) highlight that bacterial speciation is also likely to be important since common species related to the genus *Roseobacter* and other α-proteobacteria seem to be highly active in DMSPd consumption.

MODELLING DMS BIOGEOCHEMISTRY

From the discussion so far it is clear that in the past 10 years our knowledge of the processes that affect DMS production from phytoplankton DMSP has increased very significantly, and it seems likely that most of the key processes have been identified. However, it remains hard to determine experimentally which processes dominate in natural marine waters for 2 main reasons. Firstly techniques used for quantifying different processes are not necessarily compatible e.g. different experimental time scales, dark incubation rather than natural light, seawater screened for larger zooplankton or left whole. Secondly, even with the range of techniques currently available, a comprehensive field study needs a large research ship and scientific crew. Such studies are logistically demanding and extremely expensive to mount. Nevertheless very good data sets and insight into DMS production can be gained. A series of DMS biogeochemistry papers published in Deep-Sea Research Part II in 2002 are an excellent example of such a study where a developing coccolithophore bloom was labelled with SF_6 and followed for 6 days (see overview by Burkill et al., 2002). Over this period microzooplankton grazing converted most of the DMSPp to DMSPd with little DMS production, bacterial consumption dominated DMSPd turnover with 16% at most converted to DMS, bacteria also removed 62-98% of the DMS, the flux of sulphur to the air accounted for 10% of the water column DMS production and 1.3% of the DMSPp production, and the total DMS turnover time was estimated at 0.4-1.6 days (Archer et al., 2002a). To further explore DMS/P production in this *E. huxleyi* bloom, the authors went on to incorporate their DMS biogeochemistry data into an existing 1-D ecosystem model and use sensitivity analysis to

investigate the relative importance of various processes. This underlined the importance of grazing as a mechanism for the release of dissolved organic matter, and bacterioplankton production in determining the yield of DMS from DMSP. Archer et al. (2002a) concluded that the DMS yield (i.e. the point at which DMS is produced in the pathway from DMSPp to DMS) can be variable even within the progression of a single bloom. The yield being greatest when DMS is produced directly via phytoplankton cell lysis or when cells are grazed, and lower DMS production occurs when the bacterioplankton demand for DMSP-sulphur is high.

There have been many other attempts to model and predict DMS emissions to the atmosphere. This facet of the DMS research area is moving very rapidly and we look forward to further developments! We will consider just a few key studies here. Kettle et al. (1999) and Kettle and Andreae (2000) compiled over 15,000 DMS data points to construct global DMS maps and interpolated these with respect to other published data and knowledge of biogeochemical provinces. Such databases are a fantastic resource for DMS modelling research, though utility can be limited by the inherent under-sampling of some areas and during the autumn and winter seasons. Anderson et al. (2001) extended the Kettle data base by merging it with additional data and developed a 'broken-stick' regression equation which predicts DMS from gridded chlorophyll, light and nutrient values. The patterns of DMS distribution derived from this were consistent with observations for high latitude, upwelling and shelf areas, but did not work so well for low-DMS concentration regions.

Gabric et al. (2001) extended their previous modelling analysis of DMS production in the Subantarctic Southern ocean where biogenic sulphur dominates (Gabric et al., 1998) with the aim of simulating and evaluating the DMS-climate link. They used a full ocean-atmosphere coupled general circulation model to force a DMS production model, and the results suggest a 1-6% increase in DMS flux between 1960 and 2080. An increased flux of this size would result in a –0.3 Wm^{-2} radiative forcing alongside a tripled-CO_2 forcing of +6.9 Wm^{-2}, i.e. a negative feed-back, though the analysis assumes no changes in marine food web structure over the period. Taking a somewhat similar approach, and using data obtained during several cruises, Bopp et al. (in press) derived a global DMS distribution similar to contemporary observations for a 1 x CO_2 scenario, and at 2 x CO_2 the model predicted a +2% average change, though spatial heterogeneity was large (-15 to +30%). Aumont, et al. (2002) present a model of the global distribution of DMS concentration which uses relationships formulated with Atlantic data sets applied to an update of the Kettle data set. This model was added into an existing global ocean carbon cycle model and predicted DMS and DMSPp concentration fields compared reasonably well with observations, apart from an underestimation of seasonal variability in the high latitudes. Interestingly the Aumont model indicates that ~30% of the global DMS flux occurs in the subtropical/subpolar frontal zone of the Southern Ocean, and that the area south of the Polar Front is a modest source of DMS

Finally building on initial results which suggested a relationship between vertical mixing and DMS production (Simó and Pedros-Alió, 1999) such that DMS concentration is highest when the mixed layer depth is shallow, Simó and Dachs (2002) constructed an algorithm for predicting DMS concentration from satellite chlorophyll and climatological physical data. The inverse relationship they find between DMS concentration and mixed layer depth appears to hold for ~80% of the global ocean. Previous attempts to model DMS production from chlorophyll have been less successful because of the taxonomic variability in DMSP production and the critical role of grazers, viruses and bacterial activity in DMS production. Simó and Dachs (2002) assert that their simplistic approach works because the combination of chlorophyll and mixed layer depth shifts the control on DMS production away from phytoplankton to the interaction between the microbial food web and the physical environment. Hence, it side-steps the need for accurate knowledge of all the DMS production processes and their interaction.

SIGNIFICANCE OF DMS PRODUCTION BY COCCOLITHOPHORES

It is clear that at the present time we have very scant knowledge about the DMS and DMSP production potential of coccolithophores other than the cosmopolitan *E. huxleyi*. Hence, in attempting to assess the significance of DMS production by this group we must focus initially on sulphur emission rates derived for *E. huxleyi* blooms. A range of DMS flux values, calculated using the Liss and Merlivat (1986) sea-to-air gas transfer parameterisation, are shown in Table 2. It should also be noted that the errors associated with calculating DMS flux rates are large and that this compilation is not a comprehensive list of reported values, though it does cover a number of different bloom and non-bloom areas in various different regions. DMS emission rates in excess of 15 μmol m^{-2} d^{-1} have been reported for *E. huxleyi* and *Phaeocystis* blooms. High DMS flux rates most often occur when high winds follow a period of calm weather and high DMS concentrations in the water column. For example the value of 44.4 μmol m^{-2} d^{-1} reported for the *E. huxleyi* bloom studied during the ACSOE Lagrangian study corresponded with windspeeds in excess of 25 km h^{-1}. Somewhat lower sulphur emission rate values of up to 7 μmol m^{-2} d^{-1} have been derived for *E. huxleyi* blooms in the Gulf of Maine and northern North Sea. These lower emission rates are more in line with the range of estimates reported for oligotrophic and mesotrophic open ocean areas. However, high 'spot' sulphur emission values have also been derived from data for the Pacific, Indian, Southern and Arctic Oceans, and the South China Sea. So high DMS emission rates are not exclusive to haptophyte blooms.

To put these values into some sort of global context we now consider the total input of biogenic sulphur to the atmosphere. There are many estimated values in the literature, but the value of 0.5 (+/- 0.33) Tmol a^{-1} for the marine biogenic flux from Bates et al. (1992) takes into account seasonal

and regional variations in DMS production. Taking the value of 3.62 x 10^8 km^2 for the area of the global ocean (Couper, 1989), this biogenic flux of sulphur would require a daily DMS emission rate of 3.78 (+/- 2.5) µmol m^{-2} d^{-1} over the whole ocean surface. This value should be compared with those given in Table 2. Using data from the Coastal Zone Color Scanner (CZCS) for the years 1979-1985 Brown and Yoder (1994 p. 7479) calculated a mean annual areal extent of coccolithophore blooms in subpolar and polar water of 1.0 x 10^6 km^2 (0.28% of the global ocean area). If we assume that this bloom area would last one month on average (Brown and Yoder., 1994) and constantly emit DMS at the high rate of 20 µmol m^{-2} d^{-1} this would input 6 x 10^{-4} Tmol of sulphur to the air. This is equivalent to 0.12% of the annual biogenic sulphur input value of 0.5 Tmol a^{-1} estimated by Bates et al. (1992). The quantity of sulphur emitted is further reduced if we take the areal value for white water as 4.42 x 10^5 km^2 (range 3.5 to 5.81 x 10^5 km^2, 44% of the CZCS value) calculated from more recent Sea-Viewing Wide Field-of-View Sensor (SeaWIFS) satellite data for 1997-2002 (Erik Buitenhuis and Christopher Brown, personal communication 2002). The cause of this reduction in apparent areal extent is currently under investigation.

To leave the discussion here would give a false impression because, as mentioned previously, the global distribution of *E. huxleyi* far exceeds the areal extent of blooms visible via satellite. A compilation of DMS flux data (Table 2) suggests that emission rates can also be significant in non-bloom areas. Coccolithophores are recognised as an important component of the tropical phytoplankton community (Haidar and Thierstein, 2001). They can alter surface alkalinity (Bates et al., 1996) and pCO_2 in the Sargasso Sea, and add to the 'ballast' effect whereby their particulate organic material sinks and leads to carbon mineralisation deep in the water column (the so-called CO_2-draw down effect). These observations emphasise the significance of coccolithophores in the carbon cycle and by extension it seems likely that they are also important for the sulphur cycle. However, more studies are needed to look at the microbial ecology of DMSP and DMS production in the open ocean to determine whether this differs from what is known for *E. huxleyi* blooms in the northern hemisphere.

DMS PRODUCTION IN THE PAST

'The farther backward you can look, the farther forward you are likely to see'
Winston Churchill

The coccolith-bearing haptophytes have one of the best fossil records of any marine phytoplankton group. From the major floristic changes and variation in coccolithophore abundance seen in marine sediment cores the primary radiation of the group is thought to have occurred 230 million years ago in the Early Jurassic (Young et al., 1994). The dominant impetus for geological studies of fossil coccoliths has been to produce stratigraphic data in order to determine sediment age for the oil industry. Whilst such work obviously continues, increasing recognition of the importance of the coccolithophores for global biogeochemistry has led to studies which aim to relate detailed

stratigraphic data (e.g. taxonomy and space and time distribution) with the paleoenvironment (Young et al., 1994). It is possible that coccolithophore speciation changes could have influenced DMS emissions to the early atmosphere and may have contributed to palaeotemperature fluctuations, but rather few studies have examined the coccolith sedimentary record as a potential proxy for DMS production. A notable exception is the study of Henriksson et al. (2000) which quantified coccoliths, alkenones and dinosterol in an equatorial Atlantic core and indicated that DMS production increased during glaciations. However, it should again be noted that because DMS is a product of the microbial ecology of the euphotic zone, the extrapolation between potential DMSP-containing phytoplankton and atmospheric DMS is not necessarily straightforward. Nevertheless, we suggest that as more information becomes available for DMS/P production by modern day coccolithophores, we will be in a much better position to exploit the full potential of this approach.

Arctic and Antarctic ice sheets contain a wealth of information on trace components of the atmosphere in past ages and the analysis of ice cores has greatly advanced knowledge of past climate change. The atmospheric oxidation products of DMS, sulphate and MSA, are readily removed from the air in wet and dry deposition via rain, snow and particles. The analysis of non-sea-salt sulphate and MSA in polar ice-cores gives a window on how atmospheric DMS levels, and by extrapolation water phase production of DMS, have fluctuated with time. MSA is particularly useful in this respect since it is considered to have no other significant air-phase sources. However, it must be emphasised that this is not a trivial task given the complex atmospheric chemistry of DMS (Ravishankara et al., 1997; Yin et al., 1990) and the considerable difficulties associated with the interpretation of ice-core data (Delmas, 1995; Pasteur and Mulvaney, 2000).

Recent Antarctic ice-core data covering 4 glacial cycles and a 420,000-year time span, suggests that DMS concentrations were about 5-fold higher during glacial periods (Eric Saltzman, personal communication 2000). Results for a Greenland ice core were not entirely in agreement with this since they gave the opposite MSA deposition pattern, but that for non-seasalt sulphate was similar. Higher ratios of MSA to non-seasalt sulphate were seen during warmer climate stages and the overall relationship with temperature was linear (Hansson and Saltzman, 1993). These data may reflect how temperature influences the branching pathway that leads to MSA production during atmospheric oxidation of DMS, and they underline the complexity of using MSA as a quantitative proxy for DMS in ice cores.

The Antarctic ice-core record is in accord with higher marine primary productivity during glaciations, when stronger atmospheric circulation and concomitant changes in ocean circulation, higher nutrient inputs from deeper mixing and increased deposition of iron-rich dust to the oceans occurred. It also agrees with the Atlantic sediment core coccolith data mentioned previously

(Henriksson et al., 2000). However, as discussed by Watson and Liss (1998) the resulting decrease in atmospheric CO_2 and increase in DMS would have led to further cooling and so a positive feedback on the climate system, not the negative feedback envisaged in the CLAW hypothesis (Charlson et al., 1987). From the phytoplankton perspective *E. huxleyi* is a 'young' species in geological terms - it first appeared in the fossil record for tropical waters about 270,000 years ago and became abundant ~80,000 years before present. It appeared to replace *Gephyrocapsa caribbeanica* (Thierstein et al., 1977). This is interesting given that the ice core data suggest significant DMS production prior to100,000 years ago and similar inferred DMS levels over the last 4 glacial cycles. While it is tempting to speculate that this suggests that *Gephyrocapsa caribbeanica* has similar DMS production characteristics, we should quickly note that there is no evidence for this in the DMS literature. It is also important to acknowledge that ice cores do not necessarily give a snapshot of the past global atmosphere, rather Antarctic cores probably reflect processes going on within the area bounded by the Antarctic Circumpolar Current and its overlying atmosphere. Diatoms are usually considered the dominant phytoplankton group in the Southern Ocean, but a recent study shows that coccolithophores are the major component of the flora in waters between 34^{o} and 57^{o} south, with *Emiliania huxleyi* highly dominant south of the Antarctic Polar Front (Eynaud et al., 1999). Winter et al. (1999) found living coccospheres of species that are considered to have a subtropical distribution in the Weddell Sea and suggested that the temperature tolerance of coccolithophores should be revisited. Studies of phytoplankton communities which combined CHEMTAX analysis of HPLC pigments and microscopy, show that haptophytes, including coccolithophores and *Phaeocystis antarctica,* are common in the Antarctic region (Wright and van den Enden, 2001).

DMS PRODUCTION IN THE FUTURE

Without the aid of a crystal ball it is hard to predict whether DMS emissions will alter significantly in the future! Nevertheless, useful insight can be gained from studies which consider past (see above), recent and projected changes in phytoplankton abundance, distribution and speciation, as well as studies addressing future DMS production more specifically. Modelling approaches for estimating possible DMS production under future climate scenarios were considered earlier in the chapter.

The availability of data from satellite sensors such as CZCS (October 1978 to June 1986) and SeaWiFS (since November 2001) has transformed our ability to observe and quantify ocean colour, and revolutionised understanding of phytoplankton populations in the sea. In a recent paper Gregg and Conkright (2002) revised CZCS data to make it compatible with the SeaWIFS record and merged both >200m water depth data sets to give a record spanning 1979 to 2000. Areas sparsely sampled by CZCS were omitted. They found similar global spatial chlorophyll

distributions and seasonal variability for the whole period, but the record indicated an overall chlorophyll decrease of about 6%. Much of this reduction was related to reduced phytoplankton growth at high latitudes, whereas chlorophyll increased in the low latitude basins and little change was observed in the mid-ocean gyres. In more recent years warmer sea surface temperatures and reduced wind stress have resulted in shallower mixed layers leading to the reduced chlorophyll levels observed in high latitudes. The authors concluded that some of the decadal changes observed reflected the biota responding to changes in climate.

In the early 1930's before the advent of ocean-viewing satellites, regular monitoring of phytoplankton speciation and abundance at the ocean basin scale was initiated by deploying the Continuous Plankton Recorder (CPR) from merchant ships over extended transects through the North Atlantic and the North Sea. The survey still operates today and it maintains true continuity of sampling by using the same basic CPR design and analysis techniques. The samples which represent 3 m^3 of seawater are analysed for colour index (a measure of phytoplankton biomass) and over 400 phytoplankton and zooplankton taxa are identified and counted (John et al., 2002). During the last decade most of the CPR regions including the more southerly areas of the Atlantic and the North Sea have shown an increase in phytoplankton abundance, but a decrease has been observed in the northern oceanic region of the Atlantic (Edwards et al., 2001; Reid et al., 1998). These decreases are thought to be due to changes in the North Atlantic Oscillation (NAO) which have shifted the centre of deep-water convection from the Greenland Sea to the Labrador Sea from 1988 onwards.

In a recent study Iglesias-Rodríguez et al. (in press) used coccolithophore bloom satellite data and climatological maps for physical and chemical variables, to develop a method whereby the spatial and temporal distribution of such blooms could be predicted. They conclude that within this century the areal coverage of coccolithophore populations in the Northern Hemisphere will decrease by as much as 50%, whilst a 5% decrease is likely in the Southern Hemisphere. A laboratory study has shown that calcification would be reduced in *E. huxleyi* and *Gephyrocapsa oceanica* in response to the 750 p.p.m.v atmospheric CO_2 level predicted for future (Riebesell et al., 2000). Under these conditions the cultures produced a substantial proportion of malformed coccoliths, but photosynthetic carbon fixation was enhanced. It is not so unusual to find coccolithophores with some malformed coccoliths in seawater samples today, but it is not known whether an increased percentage of such coccoliths would reduce the niche for this phytoplankton group. We are not aware of any experiments that have considered DMSP and DMS production under the doubled CO_2 scenario. In the natural environment increased seawater pH alters the carbonate system and doubled CO_2 would seriously perturb the carbon cycle. This could reduce any competitive advantage that coccolithophore CO_2–concentrating mechanisms confer in the contemporary ocean, and might lead to changes in the composition of phytoplankton assemblages.

In addition to ongoing CO_2 and pH changes, alterations in the quantity of UV radiation, temperature changes, increasingly windy or calm conditions changing the pattern and quantity of nutrients (e.g. iron) deposited to the sea via dust, could all potentially alter phytoplankton biomass and speciation. As discussed previously, DMSP-containing phytoplankton are a necessary prerequisite for DMS production so any shift in phytoplankton assemblages towards higher or lower level DMSP species could be significant. For instance sea surface warming would decrease turbulence and tend to reduce the niche for diatoms and select for coccolithophores, but the decreased turbulence plus acidification could increase the niche for dinoflagellates. However, because DMS is a product of the interactions of the microbial food web it is hard to predict potential DMS production with knowledge of phytoplankton biomass and speciation alone. As mentioned earlier the balance between bacterial sulphur demand relative to DMSP availability seems critical (Kiene et al., 1999), and UV radiation can reduce bacterial activity especially when the mixed layer depth is shallow (Simó and Pedros-Alió, 1999). Shenoy et al. (2002) found that MLD was a major control on water column DMS concentration in the Indian Ocean, but substantial interannual variability in DMS flux was seen which they suggested could be due to differences in windspeed and/or the composition of the phytoplankton assemblage. Marine phytoplankton generally have a better level of protection against UV than bacteria, so enhanced UV might favour DMS production via algal DLA over bacterial demethylation. Increased UV would also increase photoxidation of DMS to DMSO, and according to the antioxidant hypothesis of Sunda et al. (2002) cellular levels of DMSP and DLA might also increase.

OUTLOOK

We must emphasise that the quantity of DMS that is emitted to the atmosphere is a very small fraction of the marine DMSP plus DMS pool. Essentially the flux is a small 'leak' from the DMS biogeochemical cycle (see **Fig. 2**). However, it is not hard to imagine scenarios where small changes in phytoplankton biomass, phytoplankton speciation, geographic distribution, grazing, bacterial activity, viral lysis etc could make a significant impact on DMS emissions with knock-on effects on climate.

More than eight years have passed since one of us wrote a chapter on DMS production for Green and Leadbeater's book on 'The Haptophyte Algae' (Malin et al., 1994). In the intervening years, research on all aspects of DMS has increased in pace, but it seems that many challenges still remain. A large proportion of the current understanding of marine DMS and DMSP production is still only derived from studies on cultures and natural populations containing *E. huxleyi* and *Phaeocystis.* Research on these key species should continue, but we assert that there is a clear case for additional projects focussing on other coccolithophores and non-calcified haptophytes, and process studies in open ocean situations where phytoplankton biomass is relatively constant –

the 'non-bloom' situation. The common conjecture is that all haptophytes produce significant quantities of DMS, but as discussed here this assumption is based on a very scant data set. Some current modelling initiatives are based on separating marine phytoplankton into functional groups or biogeochemical guilds i.e. organisms that are related through common biogeochemical processes rather than being genetically related. Given current knowledge, when predicting global and regional DMS production or carbon cycling there is a tendency for *E. huxleyi* to be considered the 'typical' DMS producer and/or typical coccolithophore. While this may prove to be the case, we assert that this assumption needs to be tested experimentally in the laboratory and in the field. Additionally, it would also be worthwhile to pay greater attention to other phytoplankton groups such as the dinoflagellates and diatoms, which have received little research attention in the past. In this way a broader and clearer picture of the production of DMSP and DMS by marine phytoplankton should emerge.

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Table 1. Summary of the Keller et al. (1989a, 1989b and 1989c) data for total DMS plus DMSP for clonal coccolithophore and other haptophyte cultures expressed as equivalent cellular DMSP content and concentration data. The analysis technique used did not differentiate between extracellular and intracellular DMS and DMSP. Current clone designations and sites of isolation have been added (CCMP = Provasoli - Guillard National **C**enter for **C**ulture of **M**arine **P**hytoplankton http://ccmp.bigelow.org/. Note that the values for cultures of unidentified flagellates given in the 1989a paper were omitted.

	Original clone name and CCMP code	Current clone name and CCMP code where changed or available	Site of isolation	pg DMSP per cell	µmol DMSP per cm^3 cell volume
COCCOLITHO-PHORES	*Coccolithus neohelis* CONE	*Cruciplacolithus neohelis* CCMP298	Beach sand, Scripps, California Bight.	2.53	85.08
	Emiliania huxleyi BT6	CCMP373	Sargasso Sea	0.75	166.42
	Emiliania huxleyi 8613C	CCMP376	Gulf of Maine	1.10	124.4
	[a]*Pleurochrysis carterae* COCCOII	CCMP645	Wood's Hole, Nantucket Sound.	12.0	170.15
	[a]*Syracosphaera elongata* SE62	[a]*Pleurochrysis carterae* CCMP874	unknown	19.8	35.3
	Umbilicosphaera sibogae L1178	na	na	13.8	195.52
	unidentified 8613COCCO	na	na	1.1	125.37
OTHER HAPTOPHYTES	*Chrysochromulina ericina* NEPCC109A	CCMP281	North Pacific	3.81	251.49
	Chrysochromulina herdlansis NEPCC186	CCMP284	North Pacific	3.62	412.69
	Chrysochromulina polylepis ED1	CCMP1757	North Sea	6.14	191.79
	Chrysochromulina polylepis ED2	CCMP286	North Sea	11.7	394.78
	Imantonia rotunda IIE_6	CCMP458	Gulf Stream	0.18	159.70
	Imantonia rotunda 1197NTA	CCMP456	Gulf of Mexico	0.26	87.31
	Isochrysis galbana CISO	CCMP463	Caribbean Sea	0.50	56.87
	Pavlova lutheri MONO	na	na	0.05	3.28
	Pavlova pinguis IG_7	CCMP609	Sargasso Sea	0.71	46.87
	[b]*Pavlova* sp. IIB_3	CCMP617	Gulf Stream	0.22	53.36
	Pavlova sp. IIB_3ax	CCMP617	Gulf Stream	0.65	156.72
	[b]*Pavlova* sp. IIG_3	CCMP620	Gulf Stream	0.45	51.19
	Pavlova sp. IIG_3ax	CCMP620	Gulf Stream	0.52	59.18
	[b]*Pavlova* sp. IIG_6	na	na	0.65	73.66
	Pavlova sp. IIG_6ax	na	na	0.73	83.58
	Phaeocystis sp. 677-3	*Phaeocystis globosa* CCMP628	Caribbean Sea	2.29	260.45
	Phaeocystis sp. 1209	*Phaeocystis globosa* CCMP627	Gulf of Mexico	1.0	113.43
	Prymnesium parvum PRYM	CCMP708	unknown	1.7	111.94

[a] Name synonyms *Cricosphaera carterae* and *Hymenomonas carterae*
na = information not available
ax = axenic clones
[b] Bacteria isolated from these clones showed no detectable DMS release.

Table 2. A selection of sulphur emission rates from the literature. For comparability only values estimated using the Liss and Merlivat (1986) wind speed based sea-to-air gas exchange parameterisation are given. It should be noted that up to ~30% higher DMS flux values would be obtained if the more recent parameterisations proposed by Wanninkhof (1992), Wannikhof and McGillis (1999) or Nightingale et al (2000) were used. The whole ocean (3.62×10^8 km^2) value given is the average DMS flux needed to fulfill the estimated total marine biogenic flux of 0.5 (+/- 0.33) Tmol a^{-1} (Bates et al., 1992)

Area	**DMS flux µmol m^{-2} d^{-1} mean and/or range**	**Reference**
Whole ocean	**3.78 (+/- 2.5)**	see legend
***Emiliania huxleyi* blooms**		
North East Atlantic June-July 1991	26.9	Holligan et al. 1993
North East Atlantic June-July 1987	[a]20.7	Malin et al. 1993
Gulf of Maine July 1990	0.94 - 6.25	Matrai & Keller 1993
[b]Northern North Sea June-July 2002	6.0	Archer et al. 2002
[b]North East Atlantic June-July 1998	[c]0.24 - 44.4	Jickells et al. in prep.
***Phaeocystis* blooms**		
GB Shelf July-August 1985	29.2	Turner et al. 1988
Faeroe Islands area June-July 1987	11.4	Malin et al. 1993
Southern North Sea June 1989	16.4	Turner et al. 1996
Southern North Sea summer 1989	5.92	Turner et al. 1996
Other areas		
North Pacific 1982-1985	4.97 (2.11 – 11.84)	Bates et al. 1987
Eastern tropical Pacific February 1989	13.6 (0.5 - 36)	Kiene & Bates 1990
North East Pacific April 1991	0.8	Bates et al. 1994
Central Arctic August to October 1991	0.6 (~0 - 19)	Leck & Persson 1996
South China Sea Nov-Dec 1993	7.6 (0.19 – 20.6)	Yang et al. 1999
[d]Southern Ocean Spring-Summer 1991-1995	9.4 (1.7 – 49)	Curran & Jones 2000
Indian Ocean Jan-March 1998	1.0 (0.1 - 3.1)	Shenoy et al. 2002
Indian Ocean Jan-March 1999	7.2 (0.2 - 29.1)	Shenoy et al. 2002

[a]for area west of 10°W with high coccolithophore abundance.
[b]Lagrangian studies using sulphur hexafluoride as a tracer.
[c]Range of mean values for 9 patch surveys. The *E. huxleyi* bloom was within the cold core of an anticyclonic eddy (Read & Pollard 2001).
[d]Calculated from 7 research cruises.

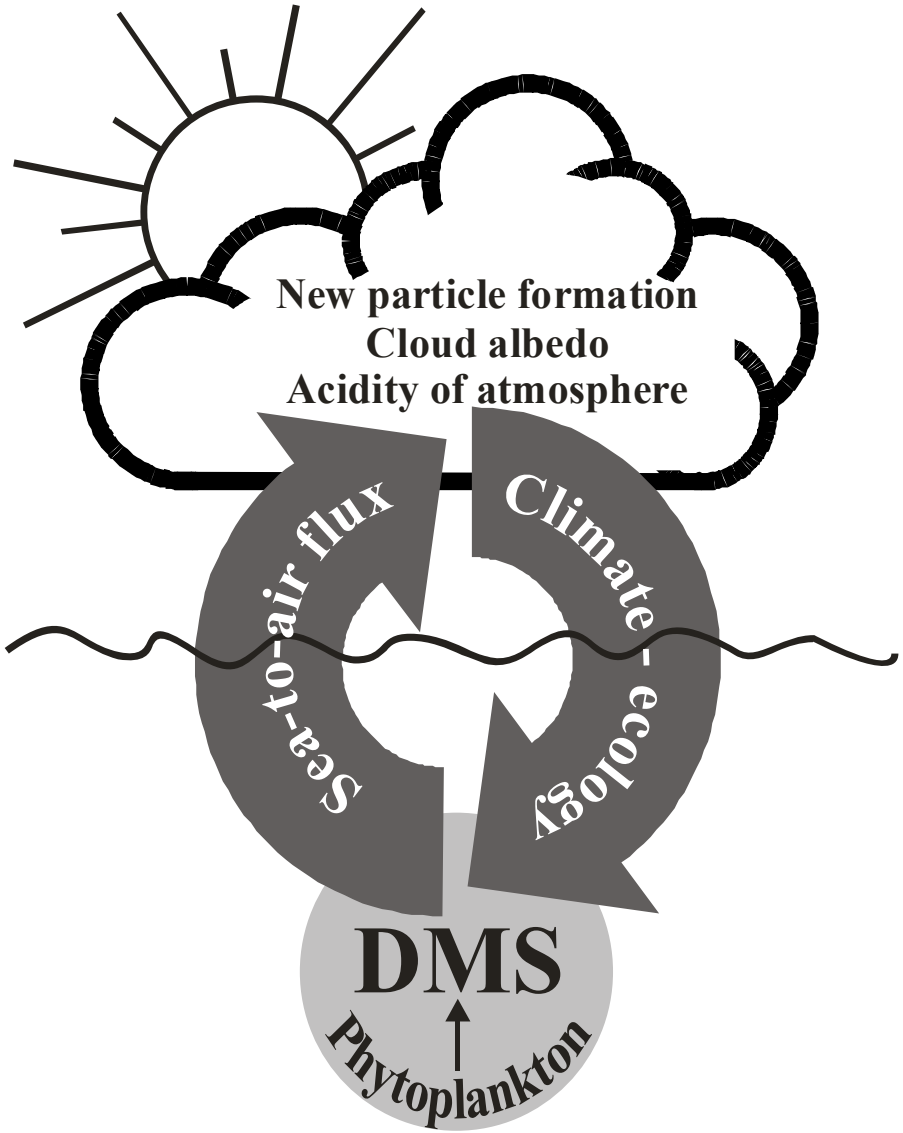

Figure 1. Research on DMS has been stimulated by the "plankton-climate connection" hypothesis of Charlson et al. (1987). DMS derived from phytoplankton is emitted to the air and is the primary source of the sulphur particles that form in the atmosphere over the remote oceans. These acidic particles stimulate cloud formation and increase the Earth's reflectivity (albedo). In turn these processes affect climate and may also influence upper ocean ecology.

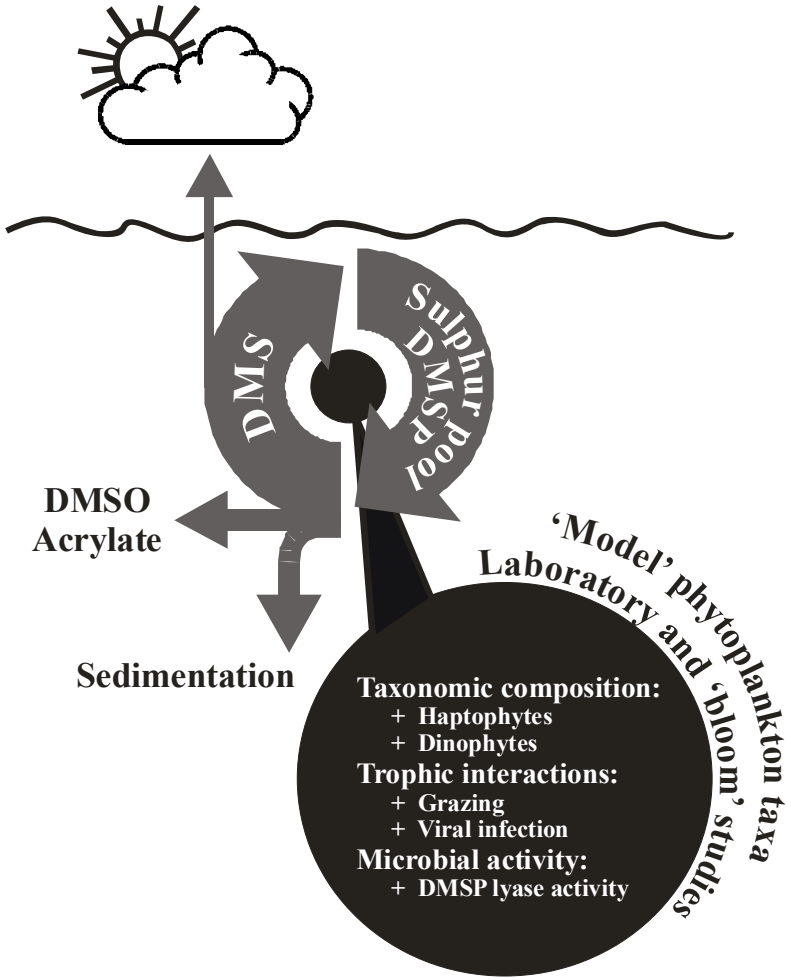

Figure 2. Current understanding of the main factors affecting the production and biogeochemical cycling of DMS. Laboratory studies with selected plankton species and field studies in phytoplankton blooms indicate rapid cycling of DMS-sulphur in the microbial food web of the upper ocean. The DMSP-DMS production wheel is driven by taxonomic composition, trophic interactions and microbial activity. Some dinophytes and haptophytes (including the coccolithophores) are recognised as important producers of DMS. Grazing by zooplankton and viral lysis can further stimulate DMS production. Losses of DMS via sedimentation, and especially sea-to-air exchange, are considered to be small relative to the total DMSP plus DMS pool, and the roles of DMSO and acrylate are not well characterised.