Marine sulphur emissions

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SUMMARY

The principal volatile sulphur species found in seawater are dimethyl sulphide (DMS), carbonyl sulphide (COS) and carbon disulphide (CS_2). Of these, DMS is the most abundant and widespread in its distribution. The predominant oceanic source of DMS is dimethylsulphoniopropionate (DMSP), a compatible solute synthesized by phytoplankton for osmoregulation and/or cryoprotection. Not all species have the same ability to form DMSP; for example, diatoms generally produce little, whereas prymnesiophytes and some dinoflagellates make significantly larger amounts. Much of the release of DMSP and DMS to the water occurs on death or through predation of the plankton. Our recent field data strongly suggest that oxidation of DMS to dimethyl sulphoxide (DMSO) is an important process in the water column, and it is clear that considerable internal cycling in the DMSP/DMS/DMSO system occurs in the euphotic zone. A fraction of the DMS crosses the sea surface and enters the atmosphere where it is oxidized by radicals such as OH and NO_3 to form products such as methanesulphonate (MSA), DMSO and non-sea salt sulphate (NSSS) particles. These particles are the main source of cloud condensation nuclei (CCN) over oceanic areas remote from land.

1. INTRODUCTION

The cycling of the element sulphur in the form of its various compounds plays many important environmental roles, particularly with respect to the atmosphere. For example, sulphur dioxide (SO_2) from both natural and fossil fuel sources is important in determining the acidity of rain and atmospheric aerosols. Following oxidation in the atmosphere, COS and CS_2 are important sources of stratospheric particles. Sulphate aerosols, derived by atmospheric oxidation of marine-derived DMS, are the main source of cloud condensation nuclei (CCN) in the marine troposphere remote from land.

Recent syntheses of our quantitative understanding of the present inter-reservoir flows in the near-surface global sulphur cycle indicate that there are considerable uncertainties in many of the estimates of the fluxes (see, for example, Moller 1995, where seven published budgets are compared). In all the budgets the two largest fluxes to the atmosphere are those from fossil fuel combustion (70–100 Tg S yr^{-1}) and from oceanic biological activity (12–58 Tg S yr^{-1}), ignoring the direct input of seawater sulphate by bubble bursting and wave breaking. The other fluxes, from volcanoes (3–9 Tg S yr^{-1}), land biosphere (0.1–7 Tg S yr^{-1}) and biomass burning (1–4 Tg S yr^{-1}), are all small in comparison. In the context of this article, the large range in the estimates of the marine biogenic source is noteworthy. Most of this flux occurs via emission from the oceans of gaseous DMS, with COS, CS_2 and hydrogen sulphide (H_2S) together accounting for $< 10\,\%$ of the total.

As the above figures indicate, currently the largest flux to the atmosphere globally is from fossil fuel combustion, which exceeds the marine biogenic flux by a factor of approximately 2–3. The dominance of man-induced inputs has been the situation for several decades, prior to which time the smaller magnitude of fossil fuel usage (vanishingly small in pre-industrial times) meant that marine emissions of DMS were the largest flux. This was probably the situation for the past several hundreds of millions of years of the Earth's history, when organisms of the type which currently produce DMS first appeared (Loeblich 1974). Looking into the future, by the turn of the millennium man-made SO_2 emissions are estimated to increase to 100–150 Tg S yr^{-1}, with much of the additional flux likely to come from coal burning in developing countries in Asia.

However, the global picture outlined above masks the fact that anthropogenic sources are more localized than natural inputs. This is illustrated in figure 1 where the relative importance of anthropogenic, biogenic and volcanic sources are compared as a function of latitude. Thus, biogenic inputs are dominant for most latitude bands in the Southern Hemisphere, whereas man-made sulphur is the major source for all latitudes in the Northern Hemisphere (Bates *et al.* 1992). Further, the rapid oxidation of anthropogenic SO_2 to sulphate and its removal from the atmosphere in rainfall and particle deposition mean that much of the impact of this source is on the regional, rather than the global scale. In

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addition, examination of source strengths tells only part of the story, for it is the atmospheric column burden that is of prime importance from the perspective of processes affected by sulphur gases and particles. Table 1 shows the results of a model calculation by Chin & Jacob (1996) which compares the percentage contributions of the three major sources in terms of both source strength and column burden. They show that the short residence time of anthropogenic sulphur in the atmosphere compared with DMS (which needs to be oxidized before it can be effectively removed) and volcanic SO_2 (often injected to high altitude compared with fossil fuel emissions) means that, according to this calculation, the majority of the sulphur in the global atmosphere at the present time comes from biogenic sources.

In view of the importance of the oceans as a source of sulphur to the atmosphere and recalling the considerable uncertainty in current estimates of the sea-to-air flux of DMS, the remainder of this paper is about the processes which control concentrations of DMS in surface seawater and its rate of transfer to the atmosphere (the major drivers of the air–sea flux). The major processes are illustrated in figure 2 and they will be dealt with in terms of factors which produce DMS and then those which destroy/transform/remove it from the water.

2. THE PRODUCTION OF DIMETHYL SULPHIDE IN SEAWATER

DMS is produced in seawater by the breakdown of its precursor, DMSP, according to the following reaction:

$$\underset{\text{Dimethylsulphoniopropionate (DMSP)}}{(CH_3)_2S^+CH_2CH_2COO^-} \rightarrow \underset{\text{Dimethylsulphide (DMS)}}{(CH_3)_2S} + \underset{\text{Acrylic Acid}}{CH_2CHCOOH}.$$

The conversion of DMSP to DMS is catalysed both intra- and extra-cellularly by the enzyme DMSP-lyase in certain phytoplankton and bacteria (Ledyard & Dacey 1996; Stefels *et al*. 1996; Steinke *et al*. 1996). The breakdown of DMSP can also be base catalysed, but at the pH and temperature of seawater the inorganic reaction is too slow to be of significance (Dacey & Blough 1987). DMSP is widely made by both macro- and micro-algae in seawater for the purposes of osmoregulation (Vairavamurthy *et al*. 1985; Dickson & Kirst 1987; Kirst 1996), cryoprotection (Karsten *et al*. 1990; Kirst *et al*. 1991; Karsten *et al*. 1996), and as a methyl donor in a variety of biochemical processes (Cantoni & Anderson 1956; Ishida 1968). There is a suggestion that the acrylic acid formed in the above reaction can also act as a bactericide (Sieburth 1961). However, more recent studies (e.g. Slezak *et al*. 1994) have concluded that acrylic acid concentrations will generally be too low to inhibit bacteria, except under special conditions where phytoplankton form aggregates such as in marine snow.

(*a*) *Relationship to pigments*

Since the production of DMSP, and hence also DMS, is intimately linked to marine phytoplankton, it has been suggested that it might be possible to estimate concentrations of these compounds from a knowledge of the distribution of chlorophyll *a*, used as a general measure of plant biomass. Such an approach would have the advantage that it would be possible to estimate DMS concentration levels in the surface oceans from the large data base for chlorophyll levels (including remote sensed ocean colour), so avoiding the need to go to the sea to measure DMS specifically. Although this has been attempted, it is generally unsuccessful since plots of DMS against chlorophyll resemble scattergrams rather than well correlated, and hence usable, relationships (Turner *et al*. 1988; Matrai *et al*. 1993). The situation is made worse by the absence until very recently of a satellite to measure ocean colour and hence chlorophyll concentrations remotely.

The reason for the generally poor correlation between DMS and chlorophyll is twofold, for not only do different phytoplankton species produce different amounts of chlorophyll, but they also differ in their ability to form DMSP, as shown in laboratory cultures by Keller *et al*. (1989). Since natural marine populations are generally of mixed species, with each one having a different DMS/chlorophyll relationship, the resultant picture shows a great deal of scatter. In those situations where one group of organisms dominates much better correlations are found, but with the slopes differing between species, as shown from samples collected at sea (Malin *et al*. 1993; Liss *et al*. 1994). These field results are in general agreement with the laboratory culture studies of Keller and co-workers, and by comparing them it is possible to draw up a crude ranking ('league table') of the ability of certain phytoplankton to produce DMSP, as follows: diatoms < *Gyrodinium* < *Phaeocystis* < *coccolithophores*; a factor of approximately 20 spanning the highest and lowest.

Understanding this large range of DMSP-producing ability may in the future lead to a way of mapping distributions of the compounds using accessory pigments, instead of the non-specific chlorophyll *a*. It is generally accepted that certain of these accessory pigments can be used as biomarkers of particular classes of phytoplankton, for example fucoxanthin in diatoms, peridinin in dinoflagellates, and 19′-hexanoyloxyfucoxanthin(19′-HEX) in prymnesiophytes (see, for example, Claustre 1994). Of particular importance in this context is 19′-HEX since prymnesiophytes, such as *Phaeocystis pouchetii* and *Emiliania huxleyi* occur near to the top of the DMSP league table. The potential utility of 19′-HEX concentrations as a surrogate for DMSP is well illustrated in figure 3. In

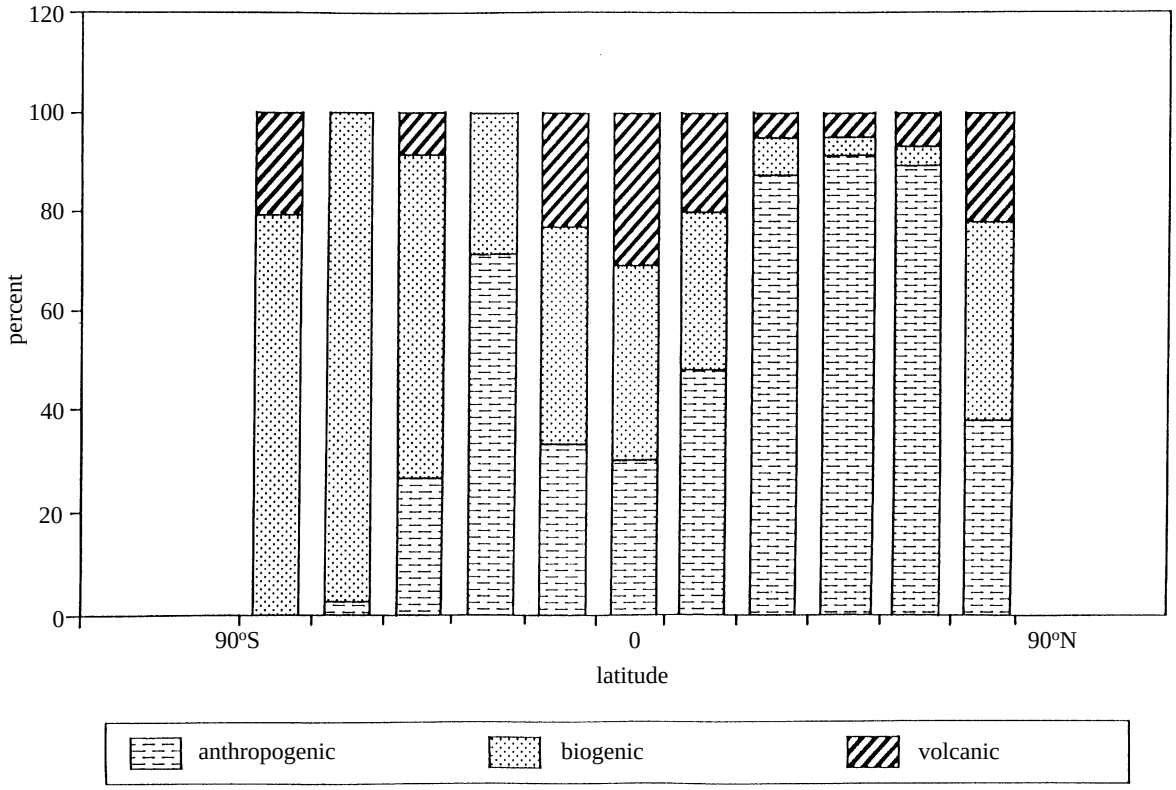

Figure 1. Latitudinal dependence of percentage contribution to sulphur emissions from anthropogenic, biogenic, and volcanic sources (after Bates *et al.* 1992).

Table 1. *Global atmospheric sulphur sources and corresponding atmospheric sulphate burdens (after Chin & Jacob 1996).*

sources	sulphate burden
total global sulphur source	96.7 (Tg S yr^{-1})
anthropogenic	67.4 (70%)
biogenic	22.6 (23%)
volcanic	6.7 (7%)
total global sulphate burden	0.53* (Tg S)
anthropogenic	0.20 (37%)
biogenic	0.22 (42%)
volcanic	0.10 (18%)

* Oxidation of COS accounts for 0.016 Tg S (3%) of the global sulphate burden, mainly in the stratosphere.

the upper panel of the figure total reduced sulphur (both dissolved and particulate DMSP plus DMS) is plotted against chlorophyll *a* for samples from the north-east Atlantic and from Antarctic waters and sea ice. The results are quite scattered, as expected. In the lower panel the same samples are plotted as total reduced sulphur against 19′-HEX, when a much clearer relationship is apparent. The relationship between DMS and 19′-HEX appears less clear-cut from a study in Antarctic waters (DiTullio & Smith 1995). If in the future there is an ocean colour satellite sensor capable of detecting accessory pigments such as 19′-HEX, then this will open up the possibility of mapping DMSP distributions from space (and maybe DMS also).

(*b*) *Relationship to nutrients* (*and temperature and light*)

Before dealing with the role of nutrients, it should be remarked that in this paper we do not deal at any length with the effects of light and temperature. This is not because they are unimportant; they are clearly fundamental factors controlling the growth of marine algae. However, there has been almost no study of the effects of these variables on the production by marine phytoplankton of DMSP and DMS specifically. The one study we know of in which the role of light intensity was examined produced ambivalent results (Vetter & Sharp 1993). These authors found that although a ten-fold increase in light intensity led to an elevation in the DMS production rate in cultures of the diatom *Skeletonema costatum* over an 18 d period, when normalized to DMS production per cell there was no consistent difference between the light treatments.

Turning now to the role of nutrients, we note that the structure of DMSP (see earlier) is similar to that of the nitrogen-containing osmoregulatory compound glycine betaine, $(CH_3)_3N^+CH_2COO^-$ (GBT), which has nitrogen as the central atom in contrast to the sulphur in DMSP. Andreae (1986) has suggested that marine plankton may produce DMSP in preference to GBT under conditions of limited nitrogen availability. Although there is some evidence for this hypothesis from laboratory culture experiments (Turner *et al.* 1988; Grone & Kirst 1992; Kiene & Service 1993; Macdonald *et al.* 1996), data from field studies are notably limited (Turner *et al.* 1988), and the relevance

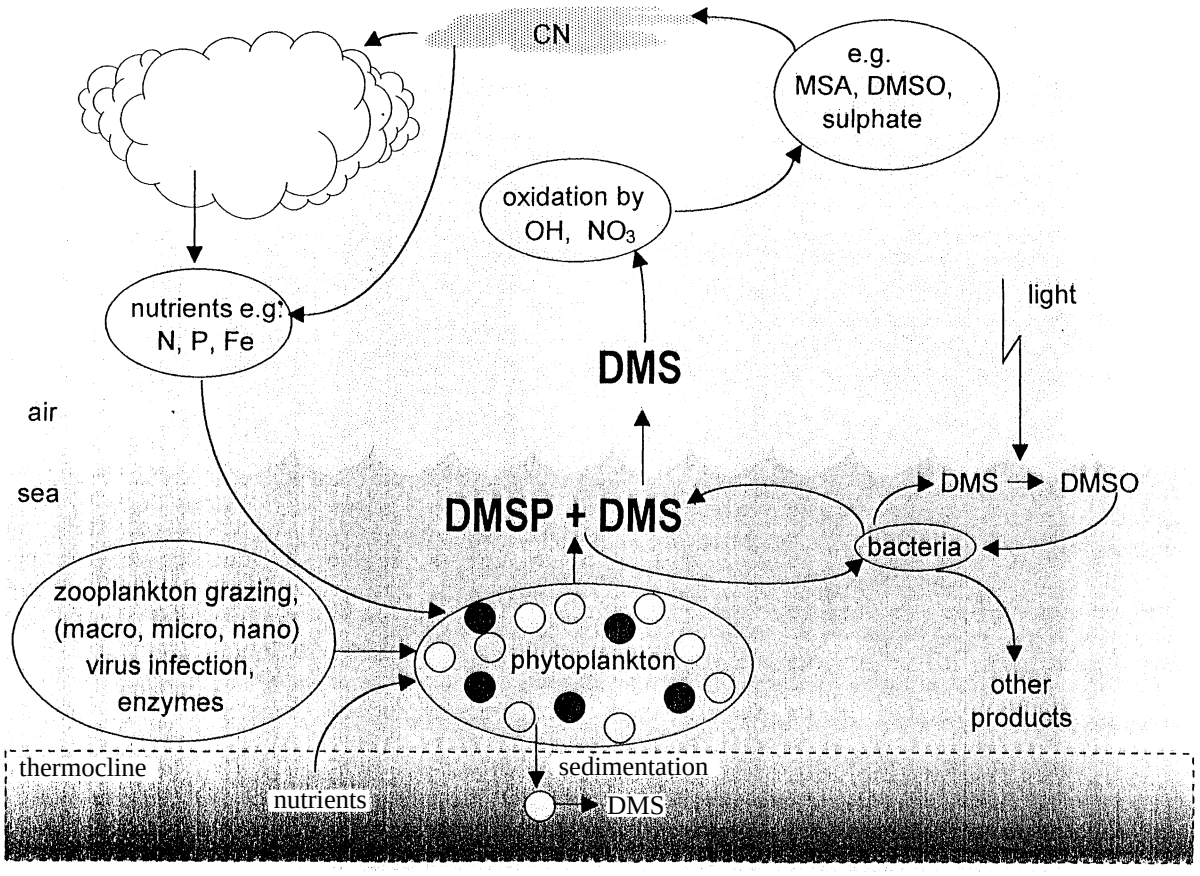

Figure 2. The cycle of marine biogenic sulphur in the ocean and atmosphere.

of the idea in the marine environment has yet to be adequately established.

A much more clear-cut example of the role nutrients can play in the production of DMSP and DMS in the oceans comes from the IRONEX I and II studies in the equatorial Pacific. In this work a patch of water approximately 100 km^2 in area was marked with an easily measurable tracer (sulphur hexafluoride, SF_6) so that it could be tracked for a period of days. Ferrous sulphate was added along with the SF_6 to test the hypothesis that iron is a limiting nutrient for plankton production in some regions of the oceans (Martin & Fitzwater 1988). Results from the two experiments indeed showed that plant production was significantly enhanced (up to 30-fold as measured by increases in chlorophyll *a* concentrations) in the iron-enriched patch, as compared to the (control) water outside (Martin *et al.* 1994; Coale *et al.* 1996). The findings with respect to DMSP and DMS within the iron-fertilized patch are shown in figure 4 (based on the data reported in Turner *et al.* 1996), which shows that both DMSP and DMS increase significantly as a result of the iron-enhanced production. Two points should be noted. First, particulate DMSP started to increase within a day or two of the iron addition, whereas the increase in DMS in the water was delayed by about a further 2 d. This is probably because aqueous DMS comes from the intracellular precursor DMSP, the major release routes for which are catalysis and zooplankton grazing (discussed later), and both of these processes will follow the initial increase in primary production. It is worth noting that actively growing phytoplankton cells generally release little or no DMSP or DMS (Turner *et al.* 1988; Keller 1989). Secondly, the increases in DMSP and DMS are less than the concomitant increases in chlorophyll, since much of the iron-enhanced production was due to diatoms which are, as noted earlier, poor producers of DMSP.

The apparent role of iron in the production of DMS by phytoplankton, illustrated in figure 4, has potentially important implications for climate through the formation of sulphate CCN by oxidation of DMS emitted from the oceans. An increase in DMS production will lead to an enhanced air–sea flux of the gas and, all other things being equal, this will result in a greater number of CCN and an increase in cloud albedo. There is evidence from ice core records for elevated levels of both atmospheric iron (a major source of the element to the oceans in areas remote from the ice-free continents) and MSA/NSSS (both products of DMS oxidation in the atmosphere) during the last glaciation (Martin *et al.* 1989; Saigne & Legrand 1987).

It has been suggested that purposeful addition of iron to the oceans might be used for climate engineering in order to enhance the oceanic drawdown of carbon dioxide and so combat global warming. If such a proposal is ever seriously considered then the impact of iron addition on the DMS/CCN/cloud albedo link also needs to be understood and included in the

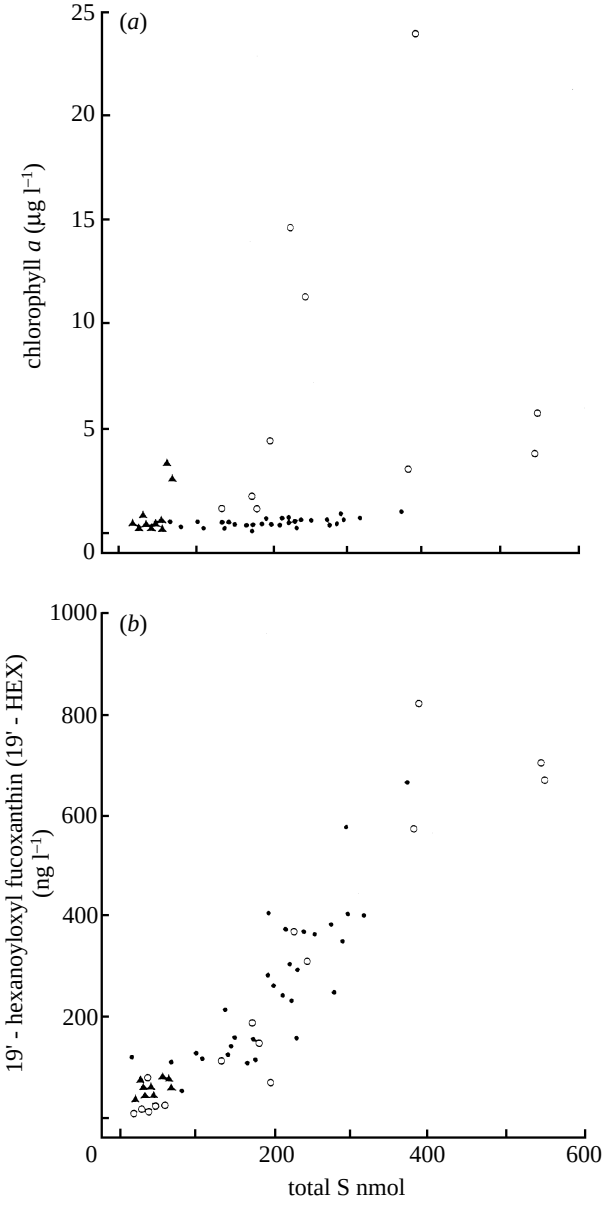

Figure 3. Total sulphur (DMSP (dissolved and particulate) and DMS) in seawater plotted against (*a*) chlorophyll *a*, and (*b*) 19′-HEX. The closed circles represent data from the north-east Atlantic, as reported in Holligan *et al.* (1993). The closed triangles and open circles are from Antarctic surface water samples and seasonal ice, respectively (Turner *et al.* 1995; Barlow *et al.* 1997).

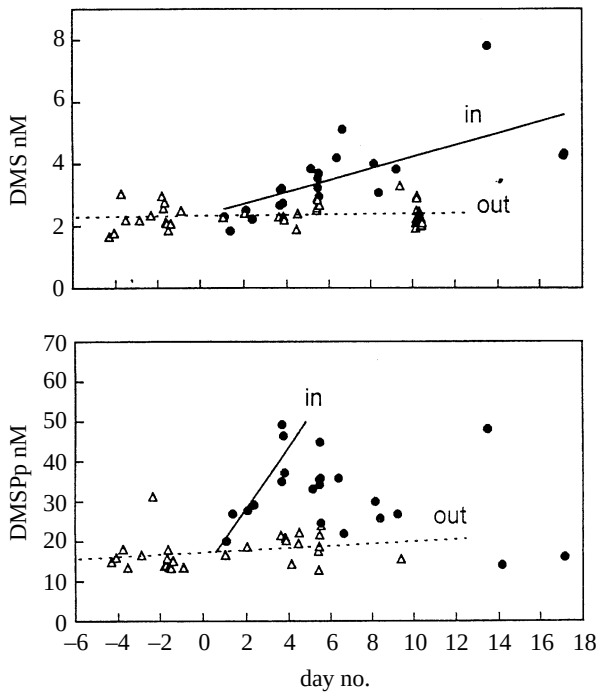

Figure 4. Temporal change in DMS (upper panel) and $DMSP_{particulate}$ (lower panel) during IRONEX (after Turner *et al.* 1996). Closed circles and open triangles represent samples taken inside and outside the iron-fertilized patch of water, respectively.

discussion. It is interesting to note that we have almost certainly already perturbed the natural iron cycle as a result of changing land use: this will have increased dust, and hence iron levels in the atmosphere, and so enhanced Fe deposition in the oceans.

In thinking about the link between iron and DMS/CCN/albedo, the Southern Hemisphere and particularly the southern oceans are a key part of the globe. The relatively small area of ice-free land in the Southern Hemisphere means that terrestrial sources of CCN are less common than in the Northern Hemisphere, and observed CCN concentrations are indeed generally low over the vast ocean areas of the Southern Hemisphere. As Twomey (1991) has shown, areas of low CCN number are much more susceptible to albedo change due to increases in particle inputs than regions where CCN numbers are already high (as in the Northern Hemisphere due to the larger land area and the inputs from industrial and urban pollution sources).

(*c*) *Effect of zooplankton grazing*

As indicated in figure 2, phytoplankton are grazed by zooplankton of various sizes, from macro (> 200 μm) through micro (20–200 μm) to nano (2–20 μm). As a result of this process the intracellular DMSP and DMS are released or repackaged at much higher rates than from actively growing cells. This was first shown by Dacey & Wakeham (1986) in laboratory culture experiments in which dinoflagellates were grazed by macrozooplanktonic copepods. We, together with colleagues at Plymouth Marine Laboratory, have carried out a laboratory study in which grazing of phytoplankton by a microzooplanktoner was shown to lead to a significant increase in the rate of release of DMS (Malin *et al.* 1994). More recent studies have been carried out by Kwint *et al.* (1996) and Daly & DiTullio (1996) in the laboratory and on board ship, respectively. In an interesting recent piece of work, Wolfe & Steinke (1996) have shown that the amount of DMS released by zooplankton grazing of *Emiliania huxleyi* is related to the amount of DMSP-lyase in the phytoplankton cells. Apparently, the effect of grazing is to 'mix' the lyase and DMSP which appeared to be otherwise separated in the growing cells.

It is useful here to mention the potentially important role of viruses in the release of DMSP and DMS, as indicated in figure 2. It was first suggested (Malin

et al. 1994) that under some circumstances viral infection can lead to the termination of a phytoplankton bloom, with consequent release of DMSP/DMS to the water (Bratbak *et al*. 1995). A dramatic example of this role for viruses comes from laboratory experiments conducted by one of us (G. M.) together with Dr Willie Wilson and Dr Nick Mann from Warwick University and Dr Gunnar Bratbak from the University of Bergen. In this study a viral strain was added to a healthily growing laboratory culture of *Phaeocystis*, which resulted in an eight-fold increase in release of DMS to the water after 48 h (Malin *et al*. 1997).

(*d*) *The removal of dimethyl sulphide from seawater*

As indicated in figure 2, there are several processes which remove (which is taken to include transform and destroy) DMSP and DMS from seawater: bacterial consumption/transformation, photochemical oxidation, and loss to the atmosphere by gas exchange across the sea surface. These are dealt with in turn. Here we ignore loss by sedimentation.

(i) *Bacterial consumption/transformation*

Reduced, methylated molecules like DMSP, DMS and DMSO represent high energy substrates for bacteria which will lead to the breakdown, transformation and interconversion of molecules of this type. A whole host of changes are possible, as indicated in figure 2 and reviewed by Taylor (1993), Kiene (1993) and Malin *et al*. (1994). The first sea-going attempt to estimate the importance of bacterial consumption/transformation of DMS was made by Kiene & Bates (1990). They incubated identical seawater samples with and without chloroform added to inhibit bacterial consumption of DMS. Addition of chloroform was assumed to have no significant effect on the production of DMSP/DMS by the phytoplankton. The results showed a wide range of biological consumption rates (spanning two orders of magnitude), but they always appear significant in comparison with other loss rates, such as air–sea exchange. There are considerable problems with the use of the chloroform inhibition technique (Wolfe & Kiene 1993*a*, *b*); further results from its use (which yield significantly lower consumption rates), and the relative importance of the results in comparison with other loss processes, are discussed later.

There is a substantial pool of DMSO in seawater, with concentrations similar to or in some cases greater than those of dissolved and particulate DMSP (Hatton *et al*. 1996). Unlike DMSP and DMS which are essentially confined to the euphotic zone of the oceans, DMSO stays at high levels in the deep oceans (Hatton *et al*. 1996). Early measurements (Andreae 1980) suffered from lack of specificity, although the development of an enzyme-linked technique (Hatton *et al*. 1994), as well as other analytical approaches (de Mora *et al*. 1993; Simo *et al*. 1996) has overcome this problem. DMSO can be formed by phototrophic bacteria (Visscher & van Gemerden 1991) or by oxidation of DMS via co-metabolism (Zhang *et al*. 1991). It can also be reduced by anaerobic bacteria to DMS (Bilous & Wiener 1985; McEwan *et al*. 1985; Clarke & Ward 1988) and used as a carbon/energy source (Debont *et al*. 1981; Suylen 1988). However, the significance of these reactions in seawater is essentially unknown. Further, DMSO can be produced photochemically in seawater, as shown originally by Brimblecombe & Shooter (1986) and discussed further later in this paper.

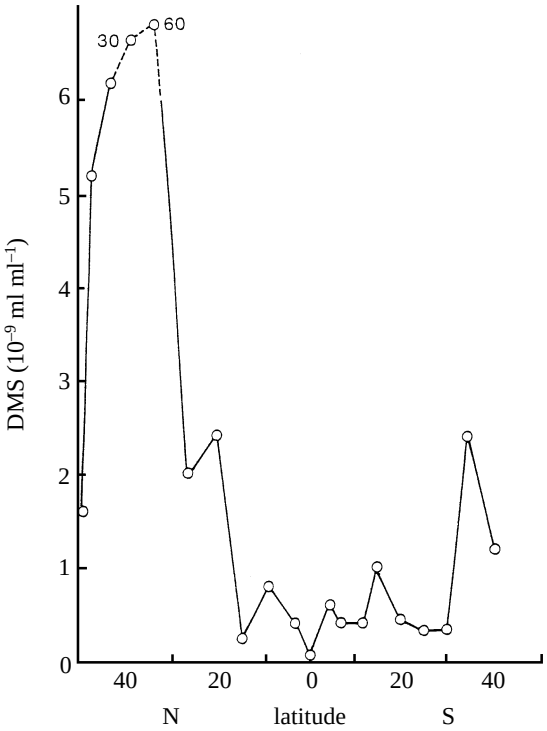

Figure 5. DMS in surface seawater in the north and south Atlantic (J. E. Lovelock personal communication and Lovelock *et al*. 1972).

The source and function of DMSO in the marine environment is not at all well established, although it has been pointed out that DMSO is a very effective cryoprotectant *in vitro* (J. E. Lovelock, personal communication). This lack of understanding of the role of DMSO reflects the present absence of detailed knowledge of how microbiological processes affect the cycling of reduced sulphur in the oceans. However, there can be little doubt that bacterial activity is likely to be of considerable importance. Interestingly, in the only published mathematical modelling study of the marine biogenic sulphur cycle (Gabric *et al*. 1993), the authors conclude that bacterial metabolism is likely to be the single most important determinant of DMS concentrations in marine surface waters.

(ii) *Photochemical oxidation*

Brimblecombe & Shooter (1986) showed in laboratory experiments that DMS in seawater could be quite rapidly photo-oxidized by sunlight with a timescale of days. The reaction was first order, and had a rate constant of about 0.09 d^{-1}, with DMSO appearing to be the sole oxidation product. Recently,

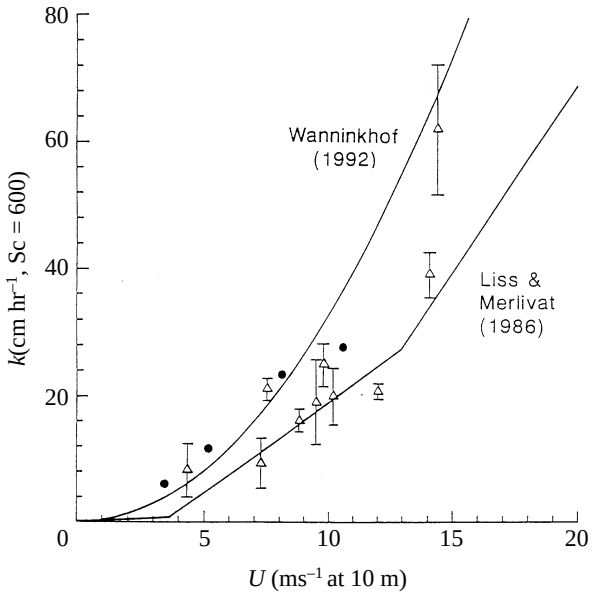

Figure 6. Transfer velocity (k), normalized to a Schmidt number of 600, as function of wind speed corrected to or measured at a height of 10 m above the water surface (from Nightingale *et al.* 1997). The theoretical predictions of the relationship between the two variables of Liss & Merlivat (1986) and Wanninkhof (1992) are also shown. The points correspond to field measurements of k made using the dual tracer technique (Watson *et al.* 1991) in the southern North Sea (triangles, Nightingale *et al.* 1997) and Georges Bank (circles, Wanninkhof *et al.* 1993).

similar experiments have been conducted on board ship by Kieber *et al.* (1996) in the equatorial Pacific. They confirmed that the reaction is first order with a rate constant of 0.05–0.15 d^{-1}, similar to that measured by Brimblecombe & Shooter. However, Kieber *et al.* found that only 14% of the DMS lost appeared as DMSO, although no other oxidation products could be identified. Maximum photolysis occurred in the wavelength range 380–460 nm. Sunlight in this wavelength range will have considerable penetration at least in clear, oligotrophic seawater, so that appreciable photolysis of DMS can be expected down to approximately 60 m.

(iii) *Air–sea exchange*

The loss of DMS from the ocean to the atmosphere is given by the product of the concentration difference across the interface, which drives the flux, and a kinetic term (often called a transfer velocity), which quantifies the rate at which the exchange takes place (Liss & Slater 1974). Since atmospheric concentrations are much smaller than those in surface seawater, it is effectively the water phase concentration of DMS which determines the driving force. Since the first oceanic determinations made by Lovelock *et al.* 1972 (shown in figure 5), many DMS concentrations in seawater have been measured. As expected for a biologically produced substance with a complex cycle of aquatic production and removal processes, the measured seawater concentrations of DMS (and its precursor DMSP) show substantial variability, both in space and time (particularly seasonally at higher latitudes). It is not possible here to review all the published data but in what is probably the most detailed study to date, Turner *et al.* (1996) were able to show for the North Sea the considerable spatial patchiness of the DMS concentration field, as well as its strong seasonality.

Turning to the transfer velocity, several formulations of this term in the flux equation have been proposed in terms of wind speed, since most of the processes controlling gas transfer are ultimately related to or controlled by wind strength. The two most widely used parameterizations are those of Liss & Merlivat (1986) and Wanninkhof (1992), see figure 6. Also given are results from a field technique for measuring the transfer velocity *in situ* by the addition of two purposefully added trace gases, ^3He and SF_6 (Watson *et al.* 1991; Nightingale *et al.* 1997). The data points generally lie between the Liss & Merlivat and Wanninkhof curves, thus giving some measure of the uncertainty in the estimation of the transfer velocity using these approaches.

3. CONCLUSIONS

The way forward in studies of the biological sulphur cycle in seawater and the emission of DMS to the atmosphere is through carefully thought-out laboratory and, especially, shipboard experiments. These should be supplemented and the results of them interpreted by mathematical modelling studies, wherever possible.

However, due to the complexity of the interactions controlling DMS concentrations in seawater, major advances in understanding will come from studies in which several of the important processes are examined together. Good examples of this approach are the Pacific sulphur/stratus investigation of Bates *et al.* (1994), and particularly the equatorial Pacific study of Kieber *et al.* (1996), discussed earlier in the section on photochemical transformations. Along with their photochemical estimates of DMS oxidation rates, Kieber *et al.* also measured DMS bacterial decomposition rates using the chloroform inhibition method, and estimated air–sea exchange fluxes from the product of DMS water concentrations and a transfer velocity. A comparison of these results is shown in figure 7 in terms of the turnover rate constant for three different thicknesses of the ocean surface layer (0–1, 0–20 and 0–60 m), with the measurements made independently on eight occasions along the cruise track. The results show that all three DMS loss mechanisms are of importance. As might be expected, in the top 1 m loss of DMS to the atmosphere is by far the dominant process. Over intermediate water thicknesses, all three loss processes were of roughly similar size. In contrast, over the full 60 m water column, bacterial consumption of DMS dominated. This finding is in general agreement with the results of Bates *et al.* (1994) who concluded from their study of competing processes in another 60 m column that loss to the atmosphere was a small fraction of the sulphur being cycled in the euphotic zone.

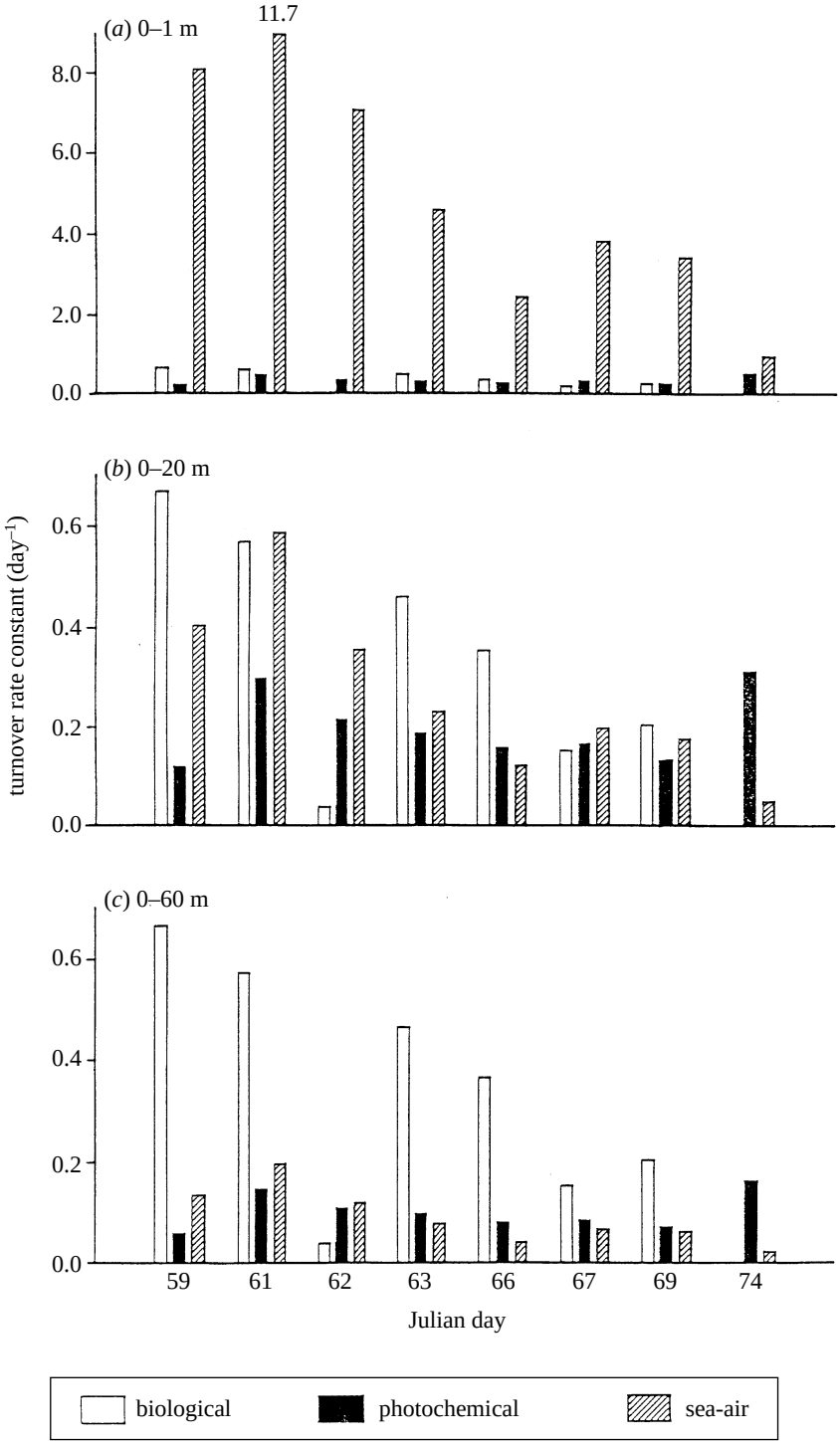

Figure 7. Comparison of the DMS turnover rate constant for photochemical, biological, and air–sea exchange processes (from Kieber *et al*. 1996). Three depth intervals are considered: (*a*) 0–1 m, (*b*) 0–20 m, (*c*) 0–60 m.

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Discussion

J. Plane (*University of East Anglia, UK*). Attempts to model the observed diurnal cycle of DMS in the equatorial mid-

Pacific boundary layer (and elsewhere) seem to require unexpectedly high OH concentrations and DMS evasion fluxes, or very low boundary layer heights. These difficulties would be ameliorated if the DMS evasion flux is not constant over a diurnal cycle, as is commonly assumed, but lower at night. In view of the complex processes involved in the production and removal of DMS within the water column, how likely is this to be the case?

P. S. Liss. Since the production process for DMS is a biological one it is certainly possible to envisage a diurnal cycle in its formation. However, in view of the complex cycle of production and destruction processes for DMS in the water, it is somewhat unlikely that a clear diurnality will be apparent. The effect has certainly been looked for at sea but there are no convincing data to prove it.