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# From cells to globe: approaching the dynamics of DMS(P) in the ocean at multiple scales[1]

**Rafel Simó**

**Abstract:** Major advances in dimethylated sulfur research are being made by approaching its dynamics at multiple scales. At the molecular to cellular level, single-cell techniques in molecular biology allow us to identify the microbes involved in cycling of dimethylated sulfur. Also, we find that dimethylsulfoxide (DMSO) is as ubiquitous as dimethylsulfoniopropionate (DMSP) in marine plankton, which supports the recent suggestion that both compounds are involved in coping with oxidative stress. At the community level, there is recent evidence for the role of DMSP as a major carrier in organic sulfur transfer and cycling through trophic levels, from phytoplankton to bacteria and to zooplankton through herbivore protozoans. As a consequence, the food web dynamics drive the oceanic emission of atmospheric sulfur. At the ecosystem level, the diverse and intricate effects of the physicochemical setting (light, wind, nutrients) on the oceanic cycling of dimethylated sulfur are being uncovered. A proposed shortcut to detailed understanding of the individual processes presents the depth of the surface mixed layer as the variable that integrates most of the environmental effects and serves for predicting dimethylsulfide (DMS) concentrations, even at the global ocean level. This opens the door to assessing the strength of the DMS biogeophysical system as a climate regulator.

**Résumé :** Des progrès importants dans la recherche sur la dynamique du soufre diméthylé se réalisent actuellement grâce à une approche à plusieurs échelles. À l'échelle moléculaire à cellulaire, des techniques utilisant une seule cellule en biologie moléculaire ont permis d'identifier les microorganismes impliqués dans le recyclage du soufre diméthylé. DE plus, le sulfoxyde de diméthyle (DMSO) est aussi omniprésent que le diméthylsulfoniopropionate (DMSP) dans le plancton marin, ce qui appuie les suggestions récentes selon lesquelles les deux composés sont impliqués dans la gestion du stress oxydatif. À l'échelle de la communauté, il y a des indications récentes que le DMSP joue un rôle comme porteur important de soufre organique dans les transferts et le recyclage à travers les différents niveaux trophiques, du phytoplancton aux bactéries et au zooplancton par l'intermédiaire des protozoaires herbivores. En conséquence, la dynamique des réseaux alimentaires contrôle l'émission du soufre atmosphérique par l'océan. À l'échelle de l'écosystème, le cadre physicochimique (lumière, vent, nutriments) a des effets divers et complexes sur le recyclage du soufre diméthylé dans l'océan. Une méthode simplifiée proposée pour la compréhension détaillée des processus individuels utilise la profondeur de la couche de mélange de surface comme la variable qui intègre le mieux la plupart des effets de l'environnement et qui sert à prédire les concentrations de sulfure de diméthyle (DMS), même à l'échelle globale de l'océan. Cela mène à une évaluation de l'importance du système biogéophysique du DMS dans le contrôle du climat.

[Traduit par la Rédaction]

## Introduction

In their seminal paper in 1987, Charlson, Lovelock, Andreae, and Warren suggested that marine phytoplankton might participate in climate regulation by the emission of volatile sulfur to the atmosphere. Such a suggestion, known as the CLAW hypothesis after the initials of the authors, was built upon the observation that the great majority of the oceanic exhalation of sulfur is in the form of dimethylsulfide (DMS). DMS is produced by degradation of the cellular component dimethylsulfoniopropionate (DMSP), which occurs in phytoplankton to fulfil important physiological functions (Kiene et al. 1996). DMSP is produced in the algal cell as a response to multiple environmental forcings and is released and degraded with involvement of the whole planktonic food web. Most of the evolved DMS, in turn, is

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**R. Simó.** Department of Marine Biology and Oceanography, Institut de Ciències del Mar (CMIMA-CSIC), Pg Marítim de la Barceloneta 37-49, 08003 Barcelona, Catalonia, Spain (e-mail: rsimo@icm.csic.es).

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degraded within the water column by microorganisms and solar radiation, and only a fraction escapes transformation to get vented into the atmosphere and become climatically active (Simó 2001).

Fifteen years after the appearance of the CLAW hypothesis, the biogeophysical–biogeochemical DMS system still draws such scientific interest that great research efforts are invested in the study of DMS and DMSP to the extent that these two tiny molecules are perhaps the organic substances for which distribution and cycling in the ocean are the best known (Simó 2001). Owing to its transversal nature across disciplines, DMS(P) research is stimulating important advances in marine science fields as diverse as the physiology and elemental composition of microorganisms, chemosensory strategies, enzymology, sulfur fluxes in food webs, photochemistry and photobiology, and air–sea exchange. Each of these research fields has its own relevant scale in time and space.

DMS(P) research reminds me of expanding circular ripples on the surface of a pond after having thrown a stone into the water: one will hardly understand the behavior of the outer rings unless one turns the sight onto the core rings and links their formation with the external forcing, the thrown stone. Likewise, we will hardly understand the global-scale dynamics of DMS and its influence on, and response to, climate unless we understand how DMSP is produced and degraded at the level of the individual cell in response to physicochemical forcing. In my opinion, the most stimulating as well as productive way of approaching DMS(P) research today is by observing how cellular controls on DMS(P) production and cycling propagate to larger scales by inclusion into community, ecosystem, and mesoscale ocean dynamics. Associated with this is the need for multidisciplinary research teams working in collaboration to address multiple scales, from molecular reactions in the cell up to the global view from satellites.

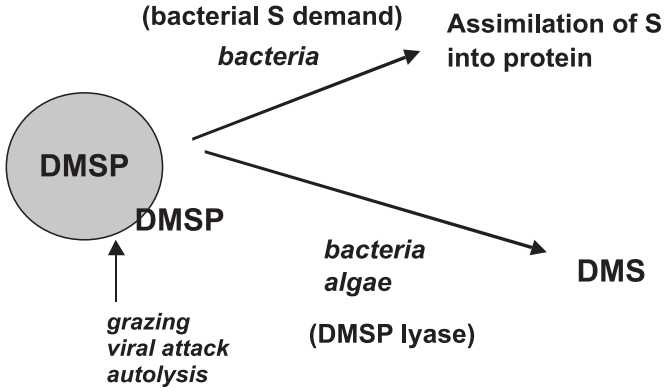
Here, I highlight several examples of recent progress in the knowledge of dimethylated sulfur dynamics at different scales. I will mainly (but not exclusively) focus on the advances made in our laboratory in collaboration with colleagues from around the world. Note that by DMS(P), I refer to DMSP and DMS together. This is not equal to referring to the dynamics of the DMSP and DMS pools summed in a single pool but to both the DMSP and DMS dynamics and their coupling. In most cases, dimethylsulfoxide (DMSO) should be included as well, but its dynamics are still too poorly known.

## Cell and population scales (micrometres to centimetres and minutes to hours)

### Unveiling the abundance and identity of DMSP-utilizing bacteria

The deeper we go into our knowledge of the many processes that comprise the biogeochemical cycle of DMS(P) in the pelagic ocean, the more complicated it appears. Some features that can be highlighted are that phytoplankton DMSP release occurs mostly through cell autolysis, viral attack, and grazing (in the latter case, a fraction of the DMSP is assimilated by the grazer). Some of the released DMSP is then converted into DMS by algal and (or) bacterial DMSP lyases, with the substrate either free in solution, attached to particles, or in the guts and vacuoles of the grazers. Exudation of DMSP or DMS by living algae is generally thought to play a minor role, though it has been suggested recently that oxidative stress may cause phytoplankton release of intracellularly produced DMS (Sunda et al. 2002). A large fraction of DMSP is utilized by bacteria through non-DMS-producing pathways as a source of reduced sulfur (Kiene et al. 2000) (Fig. 1).

**Fig. 1.** Simplified view of the fate of phytoplanktonic DMSP. The diagram is designed to stress the role of bacteria in switching between DMS- and non-DMS-producing DMSP degradation pathways. A fraction of phytoplanktonic DMSP is cleaved to DMS by algal DMSP lyases (in either healthy cells or upon lysis or grazing), as well as by bacterial DMSP lyases after release. Another (generally larger) fraction is utilized by bacteria, partly as a source of reduced sulfur. Therefore, there is a clear need to identify which bacteria do what and ask what controls their specific activity and sulfur demands.

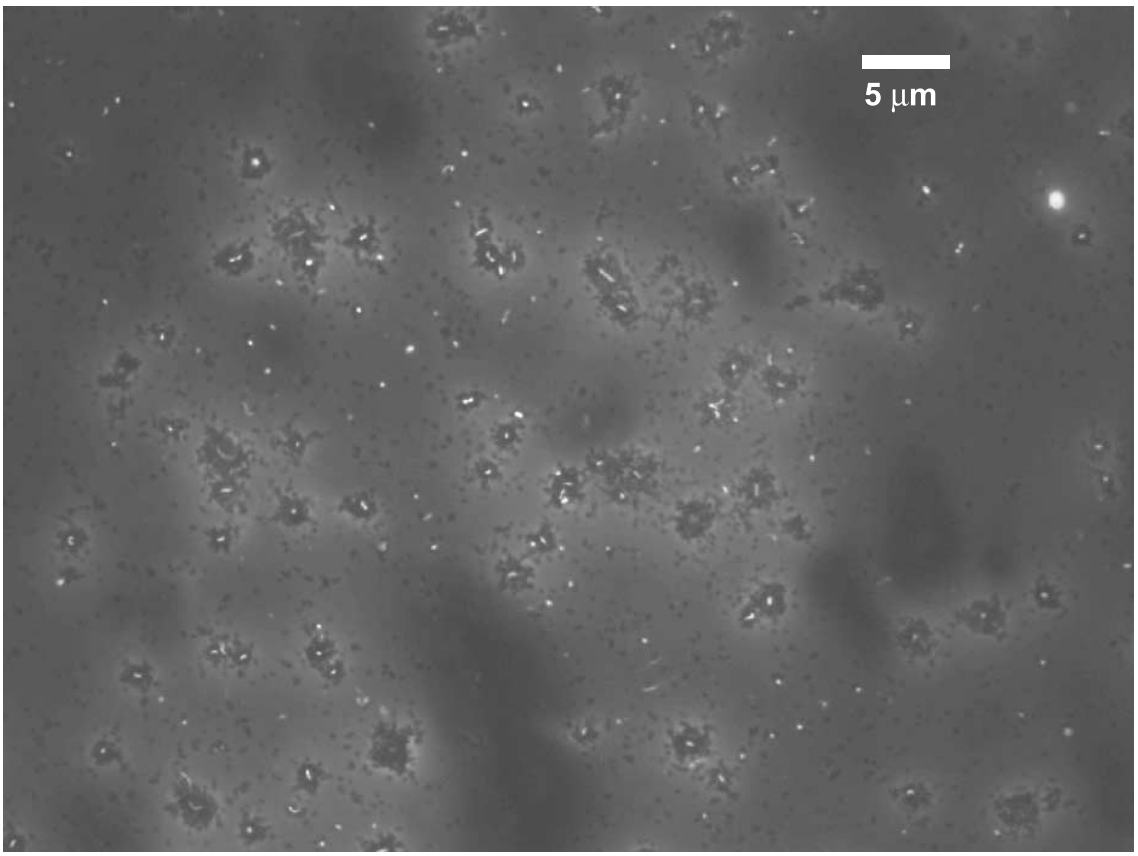



As stated by Simó (2001), a key to understand the dynamics of DMS(P) is to find out whether DMSP utilization is widespread among bacterioplankton or is a characteristic of only a few phylotypes. At present, the answer to this question is within reach thanks to the use of both classical and newly developed single-cell methods. These methods rely on the interrogation of individual cells for their activity and identity rather than measuring solely bulk activities and diversities.

We have recently applied microautoradiography (Pedrós-Alió and Newell 1989) with [$^{35}$S]DMSP to seawater samples from the coastal Gulf of Mexico enriched with inorganic nutrients (M. Vila, R. Simó, R. Kiene, J. Pinhassi, J.M. González, M.A. Moran, and C. Pedrós-Alió, unpublished data). This has allowed us to discriminate and count DMSP-assimilating cells. As many as 40–50% of the total heterotrophic bacteria associated with a DMSP-producing algal assemblage (particulate DMSP ($DMSP_p$) = 50–100 nmol·L$^{-1}$) were taking up sulfur from DMSP (Fig. 2). If these numbers are compared with those obtained simultaneously by use of a universal substrate like [$^{3}$H]leucine (60–65%), DMSP appears to be indeed an important substrate for marine bacteria.

We combined microautoradiography with fluorescent in situ RNA hybridization in a MICROFISH protocol (Lee et al. 1999) to find out the identity of those many DMSP-utilizing bacteria. Preliminary results showed that many of the cells that had taken up [$^{35}$S]DMSP belonged in the

**Fig. 2.** Epifluorescence microscopy image of marine bacteria showing the result of a microautoradiography test with [$^{35}$S]DMSP. Seawater from the coastal Gulf of Mexico was artificially enriched with inorganic nutrients to induce an algal bloom. The associated bacteria were incubated for 10 h with added [$^{35}$S]DMSP, filtered, and transferred onto a photographic emulsion. The white dots are 4′,6-diamidino-2-phenylindole stained bacterial cells. Black crowns are the marks left by the radioactive $^{35}$S on the emulsion. Thus, white dots with and without crowns are bacteria that have and have not incorporated, respectively, $^{35}$S from [$^{35}$S]DMSP (Vila et al. 2004).




*Roseobacter* phylogenetic cluster. And most of the *Roseobacter* individuals stained with the RNA probe had taken up [$^{35}$S]DMSP (Vila et al. 2004). In previous works, several lines of circumstantial evidence had pointed to *Roseobacter* (a lineage of α-*Proteobacteria* very abundant in the marine environment) as potential major players in DMSP turnover (González et al. 1999, 2000; Zubkov et al. 2001). Now, thanks to techniques such as MICROFISH, for the first time we are able to actually look for coincidence of activity and identity in every single cell. Our very preliminary results indicate that *Roseobacter* may indeed be important, but not the only, players in DMSP cycling.

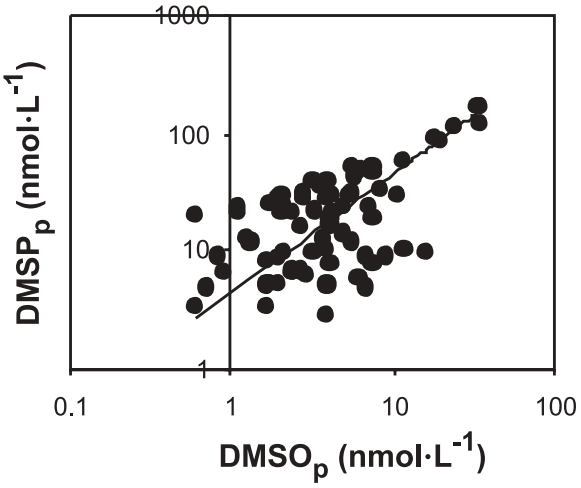
## DMSO: a forgotten intracellular sulfur pool in phytoplankton

DMSO is ubiquitous in seawater, where it contributes to the pool of dissolved organic sulfur with concentrations of the same order as those of DMS and DMSP, in some cases even higher (compilations in Simó 1998; Lee and de Mora 1999*a*). At present, the role, origins, and fate of this compound in seawater are unclear. In representations of the biogeochemical DMS(P) cycle, DMSO generally appears as a dissolved substance that acts both as a product of DMS oxidation, either photochemical (Kieber et al. 1996) or microbiological (Taylor and Kiene 1989), and as a potential biological source for DMS (Taylor and Kiene 1989). Yet, these processes have not been reliably and systematically quantified in natural samples, except for the phochemical source of DMSO, for which very few estimates exist (Kieber et al. 1996; Hatton 2002).

Simó et al. (1998) measured a pool of $DMSO_p$ in marine seston and cells of cultured phytoplankton. These results, together with the later observation of increases in dissolved DMSO ($DMSO_d$) concentration in dark seawater incubations (Simó et al. 2000), strongly suggested that eukaryotic microorganisms, mainly phytoplankton, are involved in DMSO bioproduction and release. Those preliminary reports of intracellular DMSO were accompanied with speculation about its physiological role in phytoplankton. Simó et al. (1998) and Lee and de Mora (1999*b*) suggested that DMSO could be involved in protecting the cell against photogenerated oxidants and cryogenic damage or serve as a carrier for exudation of excess sulfur and carbon through membranes.

All aerobic organisms have developed mechanisms to deal with reactive oxygen species that are produced as byproducts of photosynthesis, photooxidative stress, and respiration. In a recent paper, Sunda et al. (2002) have shown that DMSO is an effective scavenger of reactive oxygen species and suggested that this compound may join DMSP, DMS, and methane sulfinic acid in a cascade reaction system against oxidative stress. According to this hypothesis, DMSO

**Fig. 3.** Relationship between DMSP and DMSO in marine particles (GF/F retained) from the Norwegian Arctic, subpolar North Atlantic, coastal North Sea, Gulf of Maine, Sargasso Sea, subtropical Northeast Atlantic, western Mediterranean, Black Sea, and Weddel Sea (Antarctica). The mean $DMSP_p$-to-$DMSO_p$ ratio, as given by the slope of the linear regression line intercepting the 0:0 line, is 4.5 (R. Simó and M. Vila, unpublished data).




would be produced from ·OH oxidation of DMS or DMSP and, because of its hydrophilic nature, it would accumulate in the cell at the observed millimolar concentrations. Then, because of its high reactivity toward ·OH, DMSO itself would act as an efficient oxidant scavenger.

Now, we have expanded the particulate DMSO ($DMSO_p$) data set by carrying out analyses of GF/F-retained particles from a wide variety of Atlantic, Arctic, Antarctic, North Sea, Mediterranean, and Black seawaters (R. Simó and M. Vila, unpublished data). The results show that $DMSO_p$ is as ubiquitous as $DMSP_p$ in surface seawater. There is a significant positive correlation between both compounds throughout the different regions (Fig. 3), a general indication that both have a common phytoplanktonic origin.

In most of the samples, the ratio $DMSP_p$ to $DMSO_p$ falls within a range between 1 and 20, with a mean value of 4.5 (as indicated by the slope of the plot in Fig. 3). In other words, DMSO accounts for about 20% of the algal dimethylated sulfur pool (which is the far largest sulfur pool in many unicellular algae). We suggest, therefore, that $DMSO_p$ occurrence and $DMSO_d$ release have to be included in any representation of the DMS(P) cycle, and DMSO has to be considered when quantifying the fluxes of organic sulfur from phytoplankton through food chains. Both suggestions bring us to the next level, that of the whole plankton community.

## Community scale (centimetres to metres and hours to days)

### Tracking DMSP through the food web

Over the years since DMSP was discovered to occur in many phytoplankton species, the major foci for the study of this compound in the marine environment have been its role as the precursor of DMS and its physiological function in the algal cell (Kiene et al. 1996). Although some authors had observed that DMSP alone can make up >10% of intracellular carbon and >50% of intracellular sulfur in high DMSP producers (e.g., Matrai and Keller 1994), a quantitative role in the fluxes of organic matter had not been recognized, and DMSP has been regarded as a minor substance of high interest for osmoregulation and potential influence on climate. Only recently has DMSP been shown to contribute a large fraction of sulfur for heterotrophic bacterial production (Kiene et al. 1999, 2000). The mechanistic basis is the incorporation of the $CH_3S$ moiety into protein in the bacterial cell (Fig. 1). Associated with this finding was the suggestion that a large fraction of algal DMSP sulfur would be returned up the food web by means of the microbial loop through bacterial biomass (Kiene et al. 2000).

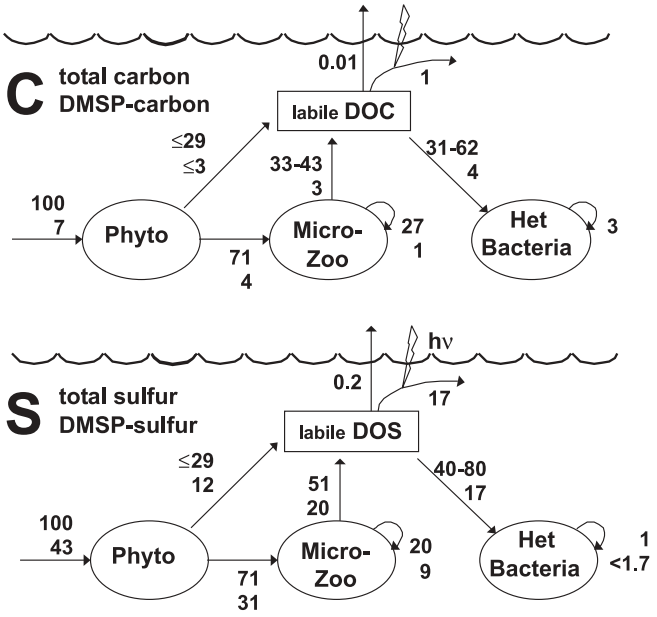
In the last 5 years, two open-sea experiments have addressed the quantitative role of DMSP in carbon and sulfur fluxes through whole microbial food webs (Simó and Pedrós-Alió 1999*a*; Burkill et al. 2002). These experiments had the common characteristics of a Lagrangian approach and the gathering of comprehensive teams. For the first time, the contributions of phytoplankton, bacteria, and grazers to DMS(P) cycling were measured simultaneously (Burkill et al. 2002; Simó et al. 2002). Both studies happened to pick up similar food webs dominated by high DMSP producing algae, and both studies showed that the contribution of DMSP and derivatives to carbon and sulfur demands was significant for all three trophic levels.

In subpolar North Atlantic waters dominated by the coccolithophore *Emiliania huxleyi* in the month of June, Simó et al. (2002) estimated that DMSP was the fate for 7% of carbon fixation through photosynthesis in phytoplankton >5 μm and accounted for 8–15% of the bacterial carbon demand and 5% of the net microzooplankton carbon production. The numbers were much higher for sulfur: DMSP and derivatives constituted 71% of algal organic sulfur, provided enough reduced sulfur to sustain all bacterial sulfur demand, and supplied 48% of the sulfur demand of microzooplankton. I show plots of the estimated contribution of DMS(P) to carbon and sulfur fluxes through the microbial food web as encountered in this Lagrangian study (Fig. 4). Values are normalized to every 100 mol of carbon and sulfur assimilated in primary production.

In the northern North Sea in June, with the phytoplankton assemblage dominated by high DMSP producers like dinoflagellates and *E. huxleyi*, Burkill et al. (2002) obtained similar results to those of the North Atlantic study. Potential $DMSP_p$ production in terms of algal carbon amounted to 7% of the $^{14}C$ production (Archer et al. 2002*a*), microzooplankton played a major role in mobilizing algal DMSP, and this compound satisfied a large fraction (30–120%) of bacterial sulfur demand (Zubkov et al. 2002).

All in all, recent investigations clearly indicate that DMSP is a prominent player in pelagic sulfur and carbon biogeochemical pumps. From the perspective of sulfur biogeochemistry and food web functioning, DMSP stands out particularly as a major carrier in organic sulfur transference and cycling through trophic levels. From the perspective of the oceanic emission of atmospheric sulfur, experimental results keep showing that DMS production cannot be understood by considering phytoplankton biomass or activity alone. Although DMSP production can be proportional to

**Fig. 4.** Diagrams of the contribution of DMSP to C and S fluxes through a microbial food web in the subpolar North Atlantic. All are normalized to a C and S photosynthetic assimilation of 100 nmol·L$^{-1}$·day$^{-1}$ by phytoplankton. Within each data pair, the top number is the measured or estimated flux of total C or S and the bottom number is the measured or estimated contribution of DMSP and derivatives to that flux, all in nmol·L$^{-1}$·day$^{-1}$. Assumptions have been made to provide estimates of those fluxes that were not measured, such as direct release to the dissolved pool by phytoplankton (Phyto), bacterial growth efficiency, or bacterial S assimilation. See details in Simó et al. (2002). DOC, dissolved organic C; Zoo, zooplankton; Het, heterotrophic; DOS, dissolved organic S.




primary production in phytoplankton assemblages dominated by high DMSP producers (Simó et al. 2002), grazers and heterotrophic bacteria utilize a large fraction of DMSP on its way to DMS, and DMS itself is utilized and photooxidized, too. Eventually, the DMS that escapes the tight couplings existing between autotrophs and heterotrophs and vents to the atmosphere represents just a tiny fraction of algal DMSP production.

### Emerging role of microzooplankton in DMS(P) cycling

The observations described above and others (e.g., Wakeham and Dacey 1989; Belviso et al. 1990; Bates et al. 1994) confirm that it is the community structure and the food web dynamics that drive the DMS(P) cycle (Simó 2001). In particular, recent field and laboratory studies show that grazers play a major role in the initial loss of phytoplanktonic DMSP (Table 1). Protozoans and other microzooplankton are major grazers in the ocean (e.g., Burkill et al. 1993). In the subpolar North Atlantic, microzooplankton ingested on average 44% of the DMSPp standing stock per day, accounting for 63% of the algal DMSP loss rates, during an *E. huxleyi* bloom (Simó et al. 2002). In the northern North Sea, 57% of the DMSP standing stock loss was ingested by microzooplankton, and as much as 91% of the phytoplankton DMSP loss was mediated by micrograzers (Archer et al. 2002*a*).

Because this dominant role of microzooplankton in channeling the loss of DMSP from the algal cell, the fate of the ingested DMSP will be a key factor in DMSP dynamics. As stated by Tang and Simó (2003), the micrograzers can either strengthen or weaken the coupling between algal DMSP and DMS production. The micrograzers may act mainly by causing the release of phytoplankton DMSP into the dissolved phase (by disruption of the algal cell, ejestion, or other unknown mechanisms) and making it available to bacteria. It can also facilitate DMSP cleavage into DMS by mixing algal DMSP lyases with DMS during cell disruption or digestion (Christaki et al. 1996; Wolfe and Steinke 1996). In both cases, microzooplankton will accelerate the coupling between phytoplankton DMSP and its transformation products such as DMS. Conversely, if DMSP accumulates in the micrograzers' biomass, it can be further transferred to higher trophic levels and the coupling between DMSP and DMS productions will be weakened.

During fieldwork, Simó et al. (2002) found that 67% of the ingested DMSP was released as $DMSP_d$ and $DMS_d$, and the other 33% was assumed to be retained in the microzooplankton biomass. Burkill et al. (2002) estimated that 70% of the phytoplankton DMSP ingested by microzooplankton was released as $DMSP_d$, only a small fraction (<7%) was converted to DMS, and the fate of the remaining fraction (>23%) was unknown.

Whether protozoans accumulate ingested DMSP is uncertain, and only indirect evidence was available until the recent laboratory experiments of Tang and Simó (2003). In multitrophic level experiments with two phytoplankters (*Phaeocystis globolosa* and *Isochrysis galbana*), a dinoflagellate micrograzer (*Gyrodinium dominans*), and a copepod (*Acartia tonsa*), we observed that although much of the algal DMSP was destroyed or released during the micrograzing process, a significant portion (32–44%) was accumulated in the protozoan biomass and transferred to the higher predator (Table 1). It is likely that the DMSP uptake efficiencies reported for *G. dominans* were a transient phenomenon; however, they were enough for the algal DMSP to pass on to the next trophic level. Selective feeding of the copepod on the protozoan when offered a protozoan–alga mixture still enhanced the role of microzooplankton in transferring DMSP up the food chain (Tang and Simó 2003).

## Ecosystem scale (metres to kilometres and hours to months)

### Physicochemical forcing on DMS(P) cycling: a case of complexity

Here, I differentiate the ecosystem from the community by including in the former the geophysical context. I am particularly interested in the role that physicochemical forcing of different kinds play in controlling the dynamics of DMS(P). A number of short-term effects of meteorological (total solar radiation, UV spectrum and intensity, wind speed) and chemical (inorganic nutrients, colored dissolved organic matter) forcing on DMS-producing communities and processes have been described (see some of them in Table 2). To mention several examples, solar irradiance affects cellular DMSP levels in algae, wind speed affects the air–sea exchange of DMS, nitrogen availability might affect DMSP

**Table 1.** Recent experimental studies of the role of microzooplankton in releasing and assimilating algal DMSP.

| Herbivore protozoan | DMSP-containing phytoplankton prey | DMSP retention efficiency (%)[a] |
|---|---|---|
| *Gyrodinium dominans* | *Phaeocystis globolosa* | 44 |
| *Gyrodinium dominans* | *Isochrysis galbana* | 32 |
| Microzooplankton action | Northeast Atlantic[b] | Northern North Sea[c] |
| Algal DMSP standing stock ingested per day (%) | 43 | 57 |
| Contribution to algal DMSP loss rate (%) | 63 | 91 |
| DMSP uptake efficiency (%) | 33 | 30[d] |

[a]Calculated by budgeting DMSP in tritrophic (phytoplankter plus protozoan plus copepod) experiments in the laboratory. This retention value might be contributed by transient DMSP from the residence of the algal prey in the vacuole. After Tang and Simó (2003).
[b]Measured by dilution experiments plus budgeting over a Lagrangian time series in the field. After Simó et al. (2002).
[c]Similar approach. After Archer et al. (2002*a*) and Burkill et al. (2002).
[d]Assumed, not measured (see Burkill et al. 2002).

biosynthesis and accumulation in phytoplankton, and colored dissolved organic matter acts as a photosensitizer for the photochemical destruction of DMS.

Physicochemical forcing factors potentially operate at all stages of the DMS(P) cycle and, unfortunately for the researchers studying them, some act in opposite ways. For instance, bacterial DNA damage by UV-B may reduce both DMS production and consumption. Hence, the influence of the environmental setting on the oceanic cycling of DMS(P) stands as a nice case of "complexity in biogeochemical systems", although this hampers our ability to represent the plankton – DMS – sulfur emission chain in the form of a simple mechanistic, quantitative, and predictive model.

## DMS losses: does biological consumption always dominate?

A good example of this complexity is given by aqueous DMS losses. DMS is lost from the mixed layer principally through three different processes: (*i*) microbial transformation, (*ii*) photolysis, and (*iii*) air–sea exchange (ventilation). Depending on the time scale considered, there is still a fourth, poorly quantified sink: vertical export by mixing events. In their pioneering study in the equatorial Pacific, Kiene and Bates (1990) observed that microbial utilization was much faster than ventilation and probably also much faster than photolysis. After that work, and in the absence of reliable field measurements of the photochemical sink, the notion that bacterial consumption far controlled DMS loss held for most of the decade of the 1990s.

In 1996, Kieber et al. reported UV photooxidation in low latitudes of the Pacific, and they showed that it could be an important sink for DMS (almost as fast as bacterial utilization and significantly faster than ventilation) at the very surface waters. Because of UV attenuation within the water, the relative strength of the photochemical sink would decrease when a thicker water column was considered. Three years later, Simó and Pedrós-Alió (1999*a*) estimated average DMS photolysis rates in the mixing layer of the subpolar North Atlantic and compared them with microbial consumption and ventilation rates. The depth criterion used for such comparison was the depth of the surface mixing layer. The results obtained showed that the three major loss processes were significant and their relative intensity was variable with time in the short term (within 2 weeks). Thus, photooxidation dominated DMS sinks under conditions of high irradiance (clear skies) and very shallow mixing, whereas bacterial consumption dominated under deeper mixing and (or) cloudy skies. Even ventilation, generally considered a minor sink, became comparable with bacterial consumption in a windstorm (Simó and Pedrós-Alió 1999*a*).

Another way of looking at the several contributions to DMS loss is by budgeting measurements of DMS production rates with DMS consumption rates. Only microbial consumption rates have been systematically measured along with production rates, so that the existence or absence of a balance between both rates will illustrate the potential role of microbes as major controllers of DMS concentrations. I show a log–log plot of 65 concurrent biological DMS production and consumption rates from different authors (Fig. 5). The majority of the data points fall below the 1:1 line, i.e., DMS production generally exceeds bacterial DMS consumption. Unless we were systematically sampling under conditions of net DMS production (there is no apparent reason to think that this is the case), the plot demonstrates that the microbial sink only accounts for a fraction of the total DMS loss. The average production:consumption ratio for all data pairs is $1.9 \pm 1.4$, and the slope of the linear correlation is $1.3 \pm 0.18$ ($r^2 = 0.46$). That is, although more data need to be compiled, so far we can say that bacterial consumption amounts to on average 50–80% of DMS production, and therefore, the remaining 20–50% required to close the balance must be accounted for by the other losses (mostly photolysis and ventilation) altogether.

## Vertical mixing: integrating complexity

Several of the many individual processes that constitute the DMS(P) cycle have been and are still being studied in isolation. This provides an essential knowledge of, for example, what are the most active wavelengths for DMS photooxidation or what is the pH optimum for a DMSP lyase or what are the major products of bacterial DMSP utilization. This allows us to explore how each of these processes responds to external forcing or perturbation, e.g., how the intracellular DMSP concentration changes with changes in

**Table 2.** Potential shorter- and longer-term effects of surface vertical mixing on different parts of the DMS(P) cycle.

| Time scale | Physicochemical forcing | Agent | Receptor of the effect | Chemical– biochemical–biological–ecological effect | Effect on the DMS(P) cycle | Sign[a] | Reference(s)[b] |
|---|---|---|---|---|---|---|---|
| Short term (minutes to days) | Light exposure | UV–PAR | Phytoplankton | Inhibition of photosynthesis | Inhibition of DMSP biosynthesis | NL? | 1, 2, 3 |
| | | | | Photooxidative stress | Cellular DMSP, DMS, and DMSO contents, DMS exudation | + | 4, 5 |
| | | | Bacteria | DNA damage repair, inhibition | S and C demands, DMSP assimilation, DMS utilization | – | 6, 7, 8, 9 |
| | | | | Exoenzyme damage | Bacterial exo-DMSP lyase activity (DLA) | –? | 10 |
| | | | Phytoplankton and bacteria | Combination of all of the above | DMS yield from DMSP consumption | NL, + | 11 |
| | | UV – low visible | Dissolved | Potential quantum yields | DMS photolysis or photooxidation | + | 12, 13 |
| | Nutrient pulses | N, Fe (P?) | Phytoplankton | Acclimation to N availability | Switch from DMSP to N analogs | –? | 14, 15 |
| | | | | Oxidative stress | Cellular DMSP and DMS contents and DLA | + | 4 |
| | | | | Unbalanced growth | DMSP overflow (DLA-mediated exudation) | + | 16 |
| Longer term (days to months) | Light exposure | UV | CDOM | Production, photobleaching | DMS photolysis/photooxidation | ±[c] | 17, 18 |
| | Nutrient regime | N, P | Phytoplankton | Succession of species and sizes | Cellular DMSP content | + | 11, 19 |
| | | | Bacteria | Succession | DMSP and DMS consumption | ? | 20, 21 |
| | | | Whole food web | Succession | DMSP fluxes within the mixed layer, turnover | +? | 2, 19 |

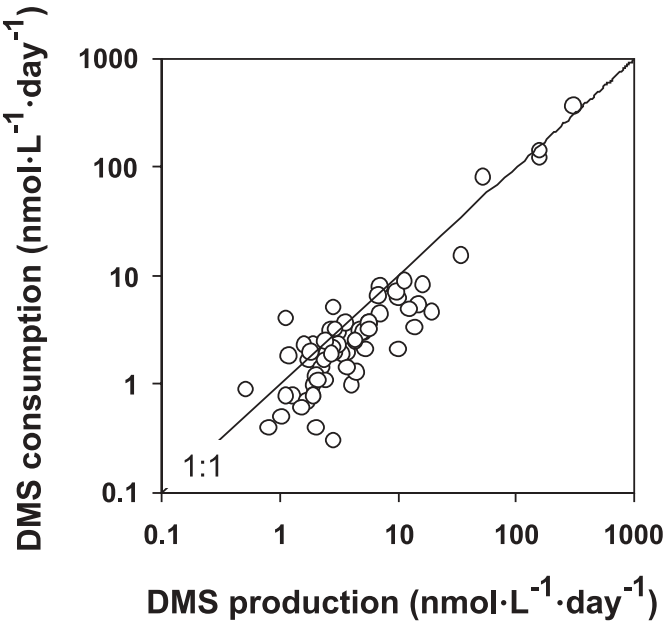
**Note:** The physicochemical forcings associated with the depth of the surface mixed layer, as well as the receptors and the non-sulfur-specific effects, are identified. The derived effects on parts of the DMS(P) cycle are either empirically observed or hypothetical. The direction of the effect with a shoaling mixed layer is also estimated. UV–PAR, UV – photosynthetically active radiation; CDOM, colored disolved organic matter.

[a]The sign estimates the direction of the effect on the DMS(P) process as forced by a shoaling in the surface MLD. +, increase; –, reduction; NL, nonlinear (sign changes with mixing depth); ?, highly uncertain because of lack of data or contradictory observations.

[b]Example references chosen to support or illustrate the suggested effect. 1, Neale et al. (1998); 2, Simó et al. (2002); 3, Archer et al. (2002*a*); 4, Sunda et al. (2002); 5, Slezak and Herndl (2003); 6, Herndl et al. (1993); 7, Jeffrey et al. (1996); 8, Kiene et al. (2000); 9, Slezak et al. (2001); 10, Yoch et al. (1997); 11, Simó and Pedrós-Alió (1999*b*); 12, Kieber et al. (1996); 13, Toole et al. (2003); 14, Andreae (1986); 15, Keller et al. (1999); 16, Stefels (2000); 17, Dacey et al. (1998); 18, Brugger et al. (1998); 19, Simó (2001); 20, Schauer et al. (2003); 21, González et al. (2000).

[c]Higher irradiances and shallower MLD in spring and summer cause both higher CDOM production and higher CDOM photobleaching. As DMS photolysis is photosensitized by CDOM, the net effect is uncertain.

**Fig. 5.** Relationship between microbial DMS consumption and production rates in 65 surface waters from the subpolar Northeast Atlantic (Simó and Pedrós-Alió 1999*a*), Barents Sea (Matrai and Vernet 1997), Labrador Sea (Wolfe et al. 1999), Gulf of Maine and Sargasso Sea (Ledyard and Dacey 1996; R. Simó et al. unpublished data), Northwest Mediterranean and coastal North Sea (van Duyl et al. 1998; Simó et al. 2000), equatorial and Northwest Pacific (Kiene and Bates 1990; Bates et al. 1994), and coastal Japan (Yang et al. 2001). All were obtained by dark seawater incubations for concurrent measurements of production and consumption, and in most of the cases, an inhibitor of DMS metabolism was used. The 1:1 line is plotted as a reference.




solar radiation intensity and spectrum. However, most of these processes are tightly interconnected, and for the purpose of gaining predictability in DMS distribution and dynamics, this complicated web of individual processes and responses becomes a maze that is hard to resolve by measurement and mechanistic modeling (Gabric et al. 2001*a*).

For this sole purpose of being able to predict surface DMS distribution under any biogeophysical conditions, we have suggested that the depth of the mixed layer (MLD) can be used as the variable that integrates most of the environmental effects, either on its own or in combination with chlorophyll *a* (Chl) concentration. The first intuition of a relationship between DMS and MLD arose a few years ago from the observation of the "summer DMS paradox": In large regions of the ocean, highest surface DMS concentrations are found in summer, when surface Chl levels are at their annual minimum and the MLD is shallowest (Simó and Pedrós-Alió 1999*b*). More recently, we have empirically found a numerical expression of this inverse relationship between DMS and MLD (see below) (Simó and Dachs 2002).

The underlying mechanistic reasons are to be found in the fact that vertical mixing/stratification controls the exposure of dissolved substances, nonliving particles, and buoyant organisms to solar radiation. It also affects phytoplankton succession and food web structure in the uppermost waters via turbulence and setting the entrainment of nutrient-rich waters. All of these effects are influential in parts of the DMS(P) cycle, as collected and summarized in Table 2. As a consequence, vertical mixing plays a key role in controlling the net production of DMS, and its quantitative expression (MLD) can therefore be used as a good predictor for surface DMS concentration.

## Global ocean scale (kilometres to global and months to decades)

### Towards global DMS prediction

If a major aim of DMS research is unraveling its link with climate, there is the unavoidable need to go global, i.e., to capture the DMS dynamics and its response to physicochemical forcing on a global scale and over months to decadal or even longer time scales (Gabric et al. 2001*a*). Like "regular" ecological models, mechanistic DMS models developed for regional studies cannot be expected to perform well at the global level.

A few semi-empirical shortcuts to global DMS prediction have been proposed. All of them have their origin in the knowledge of parts of the DMS(P) cycle but overcome a detailed understanding of the processes. Anderson et al. (2001) identified high DMS production regions as those with high light, not severe nutrient limitation, and enough decoupling between primary production and grazing. Accordingly, these authors related DMS to a proxy of the algal growth rate to produce monthly global maps of surface DMS concentration, where regions of high DMS concentration where much better represented than regions of low DMS concentration. Aumont et al. (2002) and Belviso et al. (2004) proposed a nonlinear parameterization that uses Chl concentrations and a community structure – trophic state index for DMS prediction. Underlying their relationship are the observations that DMSP occurs mostly in nano- and picophytoplankton and that DMSP is converted more efficiently into DMS when the fraction of phytoplankton contributed by the smaller algae is either very high or very low. Conceptually, this latter parameterization differs from the former in that the structure of the food web, and not only total phytoplankton growth, is taken into account. A critical evaluation of these parameterizations is given elsewhere in this issue (Vézina 2004).

A third parameterization has recently been suggested by Simó and Dachs (2002). We have derived empirical equations that relate surface DMS concentrations to Chl and the MLD as follows:

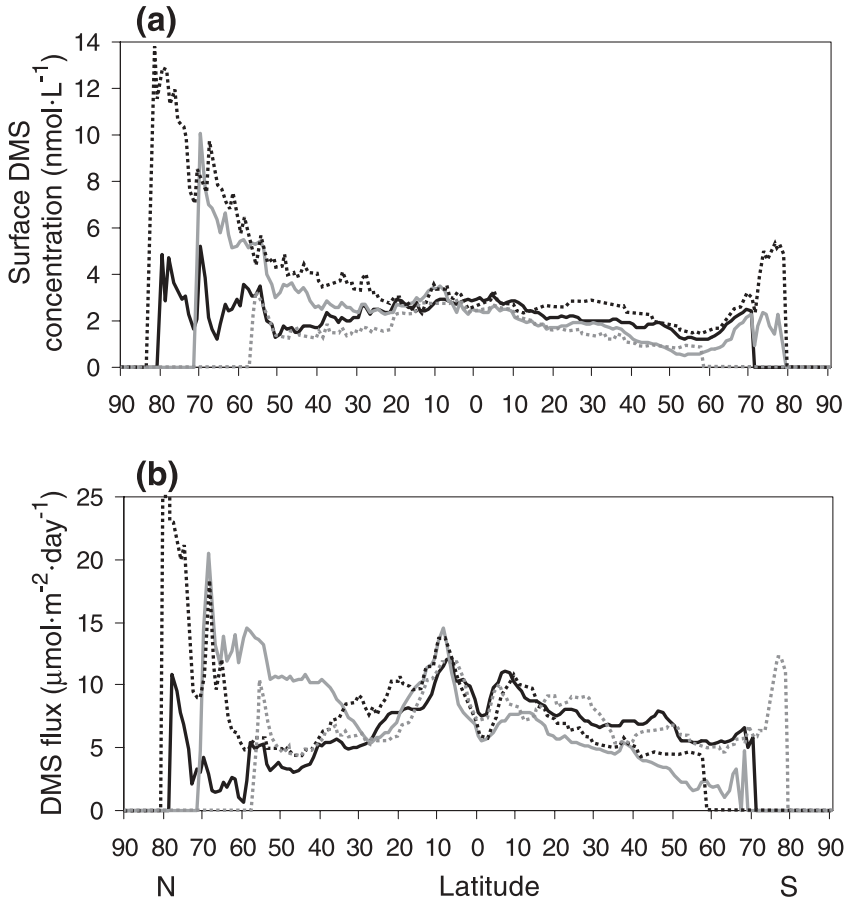
$$\mathrm{DMS} = -\ln(\mathrm{MLD}) + 5.7 \text{ if } \mathrm{Chl/MLD} < 0.02$$

$$\mathrm{DMS} = 55.8(\mathrm{Chl/MLD}) + 0.6 \text{ if } \mathrm{Chl/MLD} \geq 0.02.$$

These equations have been successfully used to predict the monthly distribution and flux of DMS in the global ocean (Fig. 6). Thus, we have found a simple empirical relationship that permits DMS concentration to be computed from measurable variables only, in particular from a combination of remotely sensed biospheric data (Chl) and climatological geophysical data (MLD).

The explanation for the good performance of this double algorithm is to be found in the "summer DMS paradox" mentioned above (Simó and Pedrós-Alió 1999*b*). An inverse

**Fig. 6.** (*a*) Monthly latitudinal averages of surface DMS concentrations in the global ocean, as predicted by the Simó and Dachs (2002) algorithm by use of climatological MLDs and satellite-derived Chl concentrations. (*b*) Monthly latitudinal averages of the sea to air emission flux of DMS, as estimated from the predicted concentrations and satellite-derived sea surface temperature and wind speed, by use of the Nightingale et al. (2000) parameterization of the air–sea exchange constant. See details in Simó and Dachs (2002). Shaded broken line, January; black line, April; black broken line, July; shaded line, October.




relationship between DMS concentration and MLD or Chl is apparent in a variety of oligotrophic regions. In more productive regions, however, high DMS levels generally accompany local high Chl levels, yet true proportionality is found only in blooms of high-DMSP-producing algae. The two equations of the Simó and Dachs (2002) algorithm indicate that high DMS concentrations occur associated not only with very high Chl concentrations but also with moderate to low Chl concentrations in shallow mixed waters, whereas deeply mixed waters exhibit low DMS concentrations. This is because shallow mixing favors blooms of DMSP-producing taxa, highly efficient DMS-producing food webs, and an array of photochemical and photobiological effects that all lead to DMS accumulation (see Table 2) (also Dacey et al. 1998; Simó and Pedrós-Alió 1999*b*; Simó et al. 2002; Simó and Dachs 2002).

## Towards linking DMS and climate

The parameterizations mentioned in the previous section allow for the desired synopticity in the global DMS distribution. They add to the climatology of existing field measurements (Kettle et al. 1999) by filling the gaps left by undersampled regions and times of the year. Moreover, these parameterizations offer predictability for projections into changing environmental conditions so that the door is open towards assessing the strength of the ocean to atmosphere sulfur flux in climate regulation.

The finding that there is an inverse relationship between DMS concentration and the MLD that holds for large regions of the global ocean surface (Simó and Dachs 2002) can be regarded as an argument in support of the CLAW hypothesis (Charlson et al. 1987), for which mechanistic explanations are still lacking. In the hypothesis, DMS emission and subsequent atmospheric oxidation affect the cloud albedo, i.e., the amount of top of atmosphere irradiance that is reflected and prevented from passing through toward ocean surface, thus affecting solar heating and probably surface wind speed as well. Since solar radiation and wind friction are the primary forcing factors that set the MLD by in-water downward fluxes of heat and turbulent energy, respectively, then a closed loop of chained effects from DMS emission to aqueous DMS through albedo and vertical mixing can be envisaged (Simó 2001).

Nonetheless, the eventual links between the DMS flux, the cloud albedo, and the MLD will not be straightforward and will depend on the time scale considered. Any change in wind speed caused by a change in albedo, for instance, will have a time-depending effect on the DMS flux. Thus, an in-

creasing wind speed increases the air–sea flux in a matter of minutes to hours, but it also deepens the mixed layer and reduces the DMS concentration and flux in the longer term (hours to days). Persistent (days to months) strong winds provide a high air–sea exchange constant but do not allow for a DMS buildup in surface waters, so that they are associated with persistent low fluxes.

Over time scales much longer than short-term wind variability (months to seasons), higher DMS fluxes will be associated with shallower MLD. If the hypothesized subsequent increase in the albedo and reduction of the heat flux occur, these should prevent MLD from further shoaling and DMS concentrations from further rising, thus closing a negative feedback loop á la CLAW. At time scales of years to decades to centuries, a persistent forcing such as the radiative effect of rising atmospheric $CO_2$ will generate a persistent response in the DMS-emitting system, which so far we have not been able to anticipate reliably. For DMS research to meet societal interests, it is crucial that we use all that we have learned in the past 15 years to predict if global warming will result in an increase or a decrease of DMS emissions, i.e., if DMS will attenuate or amplify global warming.

As DMS and its oxidation products are short-lived substances in the atmosphere, any significant influence of oceanic sulfur emission on global climate, and vice versa, has to build upon the sum of local (mesoscale) effects. Diagnostic modeling with existing or newly generated comprehensive data sets (e.g., Archer et al. 2002*b*) should help define the feasibility and proper time scale of any double-way link between DMS flux and geophysical (meteorological) perturbation on the mesoscale. However, getting beyond the mesoscale in both time and space requires the great effort of coupling biogeochemical prognostic DMS models of regional applicability (e.g., Gabric et al. 1993) to coupled general circulation models for the global ocean (CGCMs) (Grassl 2000). The problem with this is that the representation of oceanic biogeochemistry (including plankton ecology) in CGCMs is still in its low developmental stages.

While awaiting, and working towards, the evolution of prognostic models (e.g., Gabric et al. 2001*b*) applicable to the global ocean, the coupling of semi-empirical parameterizations with CGCMs (e.g., Bopp et al. 2004) is a very useful tool for assessing the role of the DMS system in past climate and foreseeing its evolution in response to global warming.

## Conclusions

After many years of fragmented research that has provided the foundations, several international teams are currently making efforts to integrate the many aspects of DMS(P) research through multiple scales. I anticipate that these efforts will be greatly rewarded. Firstly, the understanding of the complexity of this fascinating biosphere-driven ocean–atmosphere gear is now within reach. And, equally important, DMS(P) research is getting better embedded in marine and environmental sciences as it benefits from, and at the same time provides advances for, the state-of-the-art study of, e.g., food webs, theoretical ecology, physiology and phylogeny, biogeochemical cycles, aerosol chemistry, or remote sensing.

Back to the metaphor of expanding circular ripples, we understand the behavior of the outer ripples thanks to having asked the proper questions at the core ripples and vice versa. We are beginning to capture the global dynamics of DMS(P) and their role in climate because we are gaining understanding of their dynamics at smaller scales, as small as the unicellular microbe and its food web partners. Likewise, the over the years observation of the meso- and macroscale distribution of DMS(P) has allowed us to ask the right questions at the cellular level, which are yielding important advances in the knowledge of the physiology, phenology, and dynamics of marine plankton.

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## References

Anderson, T.R., Spall, S.A., Yool, A., Cipollini, P., Challenor, P.G., and Fasham, M.J.R. 2001. Global fields of sea surface dimethylsulfide predicted from chlorophyll, nutrients and light. J. Mar. Syst. **30**: 1–20.

Andreae, M.O. 1986. The ocean as a source of atmospheric sulfur compounds. *In* The role of sea–air exchange in geochemical cycling. *Edited by* P. Buat-Menard. Reidel, Dordrecht, the Netherlands. pp. 331–362.

Archer, S.D., Smith, G.C., Nightingale, P.D., Widdicombe, C.E., Tarran, G.A., Rees, A.P., and Burkill, P.H. 2002*a*. Dynamics of particulate dimethylsulphoniopropionate during a Lagrangian experiment in the northern North Sea. Deep-Sea Res. II, **49**: 2979–2999.

Archer, S.D., Gilbert, F.J., Nightingale, P.D., Zubkov, M.V., Taylor, A.H., Smith, G.C., and Burkill, P.H. 2002*b*. Transformation of dimethylsulphoniopropionate to dimethylsulphide during summer in the North Sea with an examination of key processes via a modelling approach. Deep-Sea Res. II, **49**: 3067–3101.

Aumont, O., Belviso, S., and Monfray, P. 2002. Dimethylsulfoniopropionate (DMSP) and dimethylsulfide (DMS) sea surface distributions simulated from a global 3-D ocean carbon cycle model. J. Geophys. Res. **107** (doi: 10.1029/1999JC000111).

Bates, T.S., Kiene, R.P., Wolfe, G.V., Matrai, P.A., Chavez, F.P., Buck, K.R., Blomquist, B.W., and Cuhel, R.L. 1994. The cycling of sulfur in surface seawater of the northeast Pacific. J. Geophys. Res. **99**: 7835–7843.

Belviso, S., Kim, S.-K., Rassoulzadegan, F., Krajka, B., Nguyen, B.C., Mihalopoulos, N., and Buat-Menard, P. 1990. Production of

dimethylsulfonium propionate (DMSP) and dimethylsulfide (DMS) by a microbial food web. Limnol. Oceanogr. **35**: 1810–1821.

Belviso, S., Moulin, C., Bopp, L., and Stefels, J. 2004. Assessment of a global climatology of oceanic dimethylsulfide (DMS) concentrations based on SeaWiFS imagery (1998–2001). Can. J. Fish. Aquat. Sci. **61**(5). This issue.

Bopp, L., Boucher, O., Aumont, O., Belviso, S., Dufresne, J.-L., Pham, M., and Monfray, P. 2004. Will marine dimethylsulfide emissions amplify or alleviate global warming? A model study. Can. J. Fish. Aquat. Sci. **61**(5). This issue.

Brugger, A., Slezak, D., Obernosterer, I., and Herndl, G.J. 1998. Photolysis of dimethylsulfide in the northern Adriatic Sea: dependence on substrate concentration, irradiance and DOC concentration. Mar. Chem. **59**: 321–331.

Burkill, P.H., Edwards, E.S., John, A.W.G., and Sleigh, M.A. 1993. Microzooplankton and their herbivorous activity in the northeastern Atlantic Ocean. Deep-Sea Res. II, **40**: 479–493.

Burkill, P.H., Archer, S.D., Robinson, C., Nightingale, P.D., Groom, S.B., Tarran, G.A., and Zubkov, M.V. 2002. Dimethyl sulphide biogeochemistry within a coccolithophore bloom (DISCO): an overview. Deep-Sea Res. II, **49**: 2863–2885.

Charlson, R.J., Lovelock, J.E., Andreae, M.O., and Warren, S.G. 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. Nature (Lond.), **326**: 655–661.

Christaki, U., Belviso, S., Dolan, J.R., and Corn, M. 1996. Assessment of the role of copepods and ciliates in the release to solution of particulate DMSP. Mar. Ecol. Prog. Ser. **141**: 119–127.

Dacey, J.W.H., Howse, F.A., Michaels, A.F., and Wakeham, S.G. 1998. Temporal variability of dimethylsulfoniopropionate in the Sargasso Sea. Deep-Sea Res. **45**: 2085–2104.

Gabric, A.J., Murray, C.N., Stone, L., and Kohl, M. 1993. Modeling the production of dimethylsulphide during a phytoplankton bloom. J. Geophys. Res. **98**: 22 805 – 22 816.

Gabric, A., Gregg, W., Najjar, R., Erickson, D., and Matrai, P. 2001*a*. Modelling the biogeochemical cycle of dimethylsulfide in the upper ocean: a review. Chemosphere–Global Change Sci. **3**: 377–392.

Gabric, A.J., Whetton, P.H., and Cropp, R. 2001*b*. Dimethylsulphide production in the subantarctic Southern Ocean under enhanced greenhouse conditions. Tellus Ser. B Chem. Phys. Meteorol. **53**: 273–287.

González, J.M., Kiene, R.P., and Moran, M.A. 1999. Transformation of sulfur compounds by an abundant lineage of marine bacteria in the alpha-subclass of the class *Proteobacteria*. Appl. Environ. Microbiol. **65**: 3810–3819.

González, J.M., Simó, R., Massana, R., Covert, J.S., Casamayor, E.O., Pedrós-Alió, C., and Moran, M.A. 2000. Bacterial community structure associated to a DMSP-producing North Atlantic algal bloom. Appl. Environ. Microbiol. **66**: 4237–4246.

Grassl, H. 2000. Status and improvements of coupled general circulation models. Science (Wash., D.C.), **288**: 1991–1997.

Hatton, A.D. 2002. Influence of photochemistry on the marine biogeochemical cycle of dimethylsulphide in the northern North Sea. Deep-Sea Res. II, **49**: 3039–3052.

Herndl, G.J., Müller-Niklas, G., and Frick, J. 1993. Major role of ultraviolet-B in controlling bacterioplankton growth in the surface layer of the ocean. Nature (Lond.), **361**: 717–719.

Jeffrey, W.H., Pledger, R.J., Aas, P., Hager, S., Coffin, R.B., Von Haven, R., and Mitchell, D.L. 1996. Diel and depth profiles of DNA photodamage in bacterioplankton exposed to ambient solar ultraviolet radiation. Mar. Ecol. Prog. Ser. **137**: 283–291.

Keller, M.D., Kiene, R.P., Matrai, P.A., and Belows, W.K. 1999. Production of glycine betaine and dimethylsulfoniopropionate in marine phytoplankton. I. Batch cultures. II. N-limited chemostat cultures. Mar. Biol. **135**: 237–257.

Kettle, A.J. et al. 1999. A global database of sea surface dimethylsulfide (DMS) measurements and a procedure to predict sea surface DMS as a function of latitude, longitude, and month. Global Biogeochem. Cycles, **13**: 399–444.

Kieber, D.J., Jiao, J., Kiene, R.P., and Bates, T.S. 1996. Impact of dimethylsulfide photochemistry on methyl sulfur cycling in the equatorial Pacific Ocean. J. Geophys. Res. **101**: 3715–3722.

Kiene, R.P., and Bates, T.S. 1990. Biological removal of dimethyl sulphide from sea water. Nature (Lond.), **345**: 702–705.

Kiene, R.P., Visscher, P.T., Keller, M.D., and Kirst, G.O. (*Editors*). 1996. Biological and environmental chemistry of DMSP and related sulfonium compounds. Plenum Press, New York.

Kiene, R.P., Linn, L., Gonzalez, J., Moran, M.A., and Bruton, J. 1999. Dimethylsulfoniopropionate and methanethiol are important precursors of methionine and protein-sulfur in marine bacterioplankton. Appl. Environ. Microbiol. **65**: 4549–4558.

Kiene, R.P., Linn, L.J., and Bruton, J.A. 2000. New and important roles for DMSP in marine microbial communities. J. Sea Res. **43**: 209–224.

Ledyard, K.M., and Dacey, J.W.H. 1996. Microbial cycling of DMSP and DMS in coastal and oligotrophic seawater. Limnol. Oceanogr. **41**: 33–40.

Lee, N., Nielsen, P.H., Andreasen, H., Juretschko, S., Nielsen, J.L., Schleifer, K.-H., and Wagner, M. 1999. Combination of fluorescent in situ hybridization and microautoradiography — a new tool for structure–function analyses in microbial ecology. Appl. Environ. Microbiol. **65**: 1289–1297.

Lee, P.A., and de Mora, S.J. 1999*a*. A review of dimethylsulfoxide in aquatic environments. Atmos. Ocean, **37**: 439–456.

Lee, P.A., and de Mora, S.J. 1999*b*. Intracellular dimethylsulfoxide (DMSO) in unicellular marine algae: speculations on its origin and possible biological role. J. Phycol. **35**: 8–18.

Matrai, P.A., and Keller, M.D. 1994. Total organic sulfur and dimethylsulfonio-propionate in marine phytoplankton: intracellular variations. Mar. Biol. **119**: 61–68.

Matrai, P.A., and Vernet, M. 1997. Dynamics of the vernal bloom in the marginal ice zone of the Barents Sea: dimethyl sulfide and dimethylsulfoniopropionate budgets. J. Geophys. Res. **102**: 22 965 – 22 979.

Neale, P.J., Davis, R.F., and Cullen, J.J. 1998. Interactive effects of ozone depletion and vertical mixing on photosynthesis of Antarctic phytoplankton. Nature (Lond.), **392**: 585–589.

Nightingale, P.D., Liss, P.S., and Schlosser, P. 2000. Measurements of air–sea gas transfer during an open ocean algal bloom. Geophys. Res. Lett. **27**: 2117–2120.

Pedrós-Alió, C., and Newell, S.Y. 1989. Microautoradiographic study of thymidine uptake in brackish waters around Sapelo Island, Georgia, USA. Mar. Ecol. Prog. Ser. **55**: 83–94.

Schauer, M., Balagué, V., Pedrós-Alió, C., and Massana, R. 2003. Seasonal changes in the taxonomic composition of the bacterioplankton in a coastal oligotrophic system. Aquat. Microb. Ecol. **31**: 175–182.

Simó, R. 1998. Trace chromatographic analysis of dimethyl sulfoxide and related methylated sulfur compounds in natural waters (review). J. Chromatogr. A, **807**: 151–164.

Simó, R. 2001. Production of atmospheric sulfur by oceanic plankton: biogeochemical, ecological and evolutionary links. Trends Ecol. Evol. **16**: 287–294.

Simó, R., and Dachs, J. 2002. Global ocean emission of dimethylsulfide predicted from biogeophysical data. Global Biogeochem. Cycles, **16**(4): 1078 (doi: 10.1029/2001GB001829).

Simó, R., and Pedrós-Alió, C. 1999*a*. Short-term variability in the open ocean cycle of dimethylsulfide. Global Biogeochem. Cycles, **13**: 1173–1181.

Simó, R., and Pedrós-Alió, C. 1999*b*. Role of vertical mixing in controlling the oceanic production of dimethyl sulphide. Nature (Lond.), **402**: 396–399.

Simó, R., Hatton, A.D., Malin, G., and Liss, P.S. 1998. Particulate dimethyl sulphoxide in sea water: production by microplankton. Mar. Ecol. Prog. Ser. **167**: 291–295.

Simó, R., Pedrós-Alió, C., Malin, G., and Grimalt, J.O. 2000. Biological turnover of DMS, DMSP and DMSO in contrasting open-sea waters. Mar. Ecol. Prog. Ser. **203**: 1–11.

Simó, R., Archer, S.D., Pedrós-Alió, C., Gilpin, L., and Stelfox-Widdicombe, C.E. 2002. Coupled dynamics of dimethylsulfoniopropionate and dimethylsulfide cycling and the microbial food web in surface waters of the North Atlantic. Limnol. Oceanogr. **47**: 53–61.

Slezak, D., and Herndl, G.J. 2003. Effects of ultraviolet and visible radiation on the cellular content of dimethylsulfoniopropionate (DMSP) in *Emiliania huxleyi* (strain L). Mar. Ecol. Prog. Ser. **246**: 61–71.

Slezak, D., Brugger, A., and Herndl, G.J. 2001. Impact of solar radiation on the biological removal of dimethylsulfoniopropionate and dimethylsulfide in marine surface waters. Aquat. Microb. Ecol. **25**: 87–97.

Stefels, J. 2000. Physiological aspects of the production and conversion of DMSP in marine algae and higher plants. J. Sea Res. **43**: 183–197.

Sunda, W., Kieber, D.J., Kiene, R.P., and Huntsman, S. 2002. An antioxidant function for DMSP and DMS in marine algae. Nature (Lond.), **418**: 317–320.

Tang, K.W., and Simó, R. 2003. Trophic uptake and transfer of dimethylsulfoniopropionate (DMSP) in simple planktonic food chains. Aquat. Microb. Ecol. **31**: 193–202.

Taylor, B.F., and Kiene, R.P. 1989. Microbial metabolism of dimethyl sulfide. *In* Biogenic sulfur in the environment. *Edited by* E. Saltzman and W.J. Cooper. American Chemical Society, Washington, D.C. pp. 202–221.

Toole, D.A., Kieber, D.J., Kiene, R.P., Siegel, D.A., and Nelson, N.B. 2003. Photolysis and the dimetylsulfide (DMS) summer paradox in the Sargasso Sea. Limnol. Oceanogr. **48**: 1088–1100.

van Duyl, F.C., Gieskes, W.W.C., Kop, A.J., and Lewis, W.E. 1998. Biological control of short-term variations in the concentration of DMSP and DMS during a *Phaeocystis* spring bloom. J. Sea Res. **40**: 221–231.

Vila, M., Simó, R., Kiene, R.P., Pinhassi, J., González, J.M., Moran, M.A., and Pedrós-Alió, C. 2004. Use of microautoradiography combined with fluorescence in situ hybridization to determine dimethylsulfoniopropionate incorporation by marine bacterioplankton taxa. Appl. Environ. Microbiol. **70**. In press.

Vézina, A.F. 2004. Towards modelling marine DMS production and emissions over regional and global scales. Can. J. Fish. Aquat. Sci. **61**(5). This issue.

Wakeham, S.G., and Dacey, J.W.H. 1989. Biogeochemical cycling of dimethyl sulfide in marine environments. *In* Biogenic sulfur in the environment. *Edited by* E. Saltzman and W.J. Cooper. American Chemical Society, Washington, D.C. pp. 152–166.

Wolfe, G.V., and Steinke, M. 1996. Grazing-activated production of dimethyl sulfide (DMS) by two clone of *Emiliania huxleyi*. Limnol. Oceanogr. **41**: 1151–1160.

Wolfe, G.V., Levasseur, M., Cantin, G., and Michaud, S. 1999. Microbial consumption and production of dimethyl sulfide (DMS) in the Labrador Sea. Aquat. Microb. Ecol. **18**: 197–205.

Yang, G.-P., Watanabe, S., and Tsunogai, S. 2001. Distribution and cycling of dimethylsulfide in surface microlayer and subsurface seawater. Mar. Chem. **76**: 137–153.

Yoch, D.C., Ansede, J.H., and Rabinowitz, K.S. 1997. Evidence for intracellular and extracellular dimethylsulfoniopropionate (DMSP) lyases and DMSP uptake site in two species of marine bacteria. Appl. Environ. Microbiol. **63**: 3182–3188.

Zubkov, M.V., Fuchs, B.M., Archer, S.D., Kiene, R.P., Amann, R., and Burkill, P.H. 2001. Linking the composition of bacterioplankton to rapid turnover of dissolved dimethylsulphoniopropionate in an algal bloom in the North Sea. Environ. Microbiol. **3**: 304–311.

Zubkov, M.V., Fuchs, B.M., Archer, S.D., Kiene, R.P., Amann, R., and Burkill, P.H. 2002. Rapid turnover of dissolved DMS and DMSP by defined bacterioplankton communities in the stratified euphotic zone of the North Sea. Deep-Sea Res. II, **49**: 3017–338.