

## Coupled dynamics of dimethylsulfoniopropionate and dimethylsulfide cycling and the microbial food web in surface waters of the North Atlantic

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### *Abstract*

Oceanic dimethylsulfide (DMS), the main natural source of sulfur to the global atmosphere, is suggested to play a key role in the interaction between marine biota and climate. Its biochemical precursor is dimethylsulfoniopropionate (DMSP), a globally distributed, intracellular constituent in marine phytoplankton. During a multidisciplinary Lagrangian experiment in the subpolar North Atlantic, we determined the fluxes of DMSP and DMS through phytoplankton, microzooplankton, and bacterioplankton and compared them with concurrent carbon and sulfur fluxes through primary and secondary productions, grazing, and release and use of dissolved organic matter. We found that DMSP and derivatives contributed most (48–100%) of the sulfur fluxes and 5–15% of the carbon fluxes. Our findings highlight DMSP as a prominent player in pelagic biogeochemical pumps, especially as a major carrier in organic sulfur cycling. Also, our results illustrate the key role played by microzooplankton and heterotrophic bacteria (hence the microbial food web) in controlling the amount of phytoplanktonic DMSP that ultimately vents to the atmosphere in the form of DMS.

Interest in oceanic methylated sulfur has expanded during the last decade, mostly driven by the proposed involvement of dimethylsulfide (DMS) in climate regulation. Volatile DMS produced by plankton represents a major source of reduced sulfur to the atmosphere (Andreae and Crutzen 1997). Once in the atmosphere, DMS oxidizes to form particles that, either directly or by acting as cloud condensation nuclei, scatter solar radiation, thereby influencing the Earth's radiative balance (Charlson et al. 1987; Andreae and Crutzen

1997). This is suggested to be one of the major self-regulated feedback mechanisms linking global biosphere and climate (Charlson et al. 1987). While this hypothesis is still under test, fundamental gaps exist in our understanding of the biological controls on DMS production.

DMS is produced by enzymatic cleavage of the phytoplankton component dimethylsulfoniopropionate (DMSP) that algae synthesize from methionine (Malin and Kirst 1997). DMSP is a very labile compound, and there is indication that it is transferred and transformed through the food web (Tang et al. 1999; Kiene et al. 2000; Archer et al. 2001) as a component of carbon and sulfur fluxes, with DMS as one of the byproducts of this transference chain. Hence, a key to unraveling the controls on DMS production lies in understanding the coupling between DMS and DMSP dynamics and carbon and sulfur cycling through the food web (Simó 2001). Hitherto, this has only been partly addressed due to the difficulties of measuring DMS and DMSP production and consumption rates and because of the scarcity of integrative biogeochemical studies in the open ocean.

Here we report on an integrated study of methylated sulfur cycling and food-web dynamics during an open-ocean La-

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grangian experiment in the subpolar North Atlantic. Rates of DMSP and DMS production and consumption were determined over a 4-d series together with key fluxes in the microbial food web: primary production, microbial secondary production, and microzooplankton grazing. Very few previous studies have attempted a comparative study of DMSP cycling and carbon or sulfur-based food-web processes in the open ocean (Bates et al. 1994; Matrai and Vernet 1997; Kiene and Linn 2000a). In all cases, however, only fluxes through either bacterioplankton or phytoplankton plus bacterioplankton were measured. This is the first time that simultaneous measurements of methylated sulfur fluxes through three trophic levels of the food web (phytoplankton, bacteria, and micrograzers) have been obtained. Combining these data, we have been able to evaluate the contribution of DMSP and DMS to the fluxes of carbon and sulfur in the surface mixing layer.

## Methods

*The Lagrangian time series*—The ACSOE (Atmospheric Chemistry Studies in the Oceanic Environment) North Atlantic Experiment was carried out in June–July 1998 at around 59°N, 21°W (Simó and Pedrós-Alió 1999a). The cold core of an anticyclonic eddy in the region was characterized by the dominance of the coccolithophore *Emiliania huxleyi* and chlorophyll *a* levels  $<1 \mu\text{g L}^{-1}$ , while chlorophyll *a* concentrations  $>1 \mu\text{g L}^{-1}$  were recorded in the more productive surrounding waters, where phytoplankton assemblages were dominated by dinoflagellates and small flagellates. An SF<sub>6</sub> tracer patch was deployed within the eddy core, and the traced water mass was sampled in Lagrangian mode for about 2 weeks (Simó and Pedrós-Alió 1999a). Stable meteorological conditions and balanced biological state and rate variables were observed between 14 and 17 June, before a storm changed the radiation and mixing regimes. It is the data set obtained during this 4-d period that is presented and discussed as the Lagrangian phase in this paper.

*On-deck microcosm experiment*—On 3 July, surface water collected on the edge of the eddy at 59.8°N 20.6°E was used to fill a 30-liter polyethylene carboy. The carboy was kept on deck under a polyethylene sheet so that PAR intensity inside the carboy was about 50% of that at surface, i.e., it was equivalent to that at a depth of approximately 5 m. The experiment was run for 24 h under a continuous flow of surface seawater to keep the natural temperature (approximately 11°C). Water subsamples for concentrations and process rates were extracted every 4 h.

*Phytoplankton and microzooplankton biomass*—A fluorometric method was used to measure chlorophyll *a* (Chl *a*) in 90% acetone extracts of samples collected on GF/F filters (total Chl *a*) and samples prefiltered through 2  $\mu\text{m}$  and then collected on GF/F (Chl *a* in cells  $<2 \mu\text{m}$ ). The Chl *a* in cells  $>2 \mu\text{m}$  was obtained by difference. To determine the mass of carbon in DMSP-producing phytoplankton, the assumption was made that most picoalgae and cyanobacteria  $<2 \mu\text{m}$  produce very little DMSP on a biomass basis (Keller et al. 1989; M.D. Keller, pers. comm.). The Chl *a* concen-

tration in the  $>2\text{-}\mu\text{m}$  size fraction was converted to algal carbon biomass by using a C/Chl *a* (w:w) ratio of 50. This ratio has been reported for highly irradiated *E. huxleyi* cultures (Nielsen 1997).

To determine the microzooplankton abundance and composition, 250-ml water samples were fixed in acid Lugol's and analyzed in the laboratory by inverted microscopy. The microzooplankton assemblage was diverse and dominated by oligotrichous ciliates and heterotrophic dinoflagellates. Biovolumes were calculated using an image-analysis system and converted to biomass using group-specific volume:carbon conversion factors (0.19  $\mu\text{gC } \mu\text{m}^{-3}$  for ciliates; Putt and Stocker 1989; 0.14  $\mu\text{gC } \mu\text{m}^{-3}$  for dinoflagellates; Lessard 1991).

*Primary and heterotrophic productions*—Size-fractionated primary production estimates were obtained for different depths using standard JGOFS <sup>14</sup>C methodology (Savidge and Gilpin 1999). Predawn samples were collected from six depths within the euphotic zone corresponding to 97, 55, 20, 7, 5, and 1% surface irradiance. These samples were inoculated with <sup>14</sup>C sodium bicarbonate and incubated on-deck under simulated in situ light conditions for 24 h. Following incubation the samples were fractionated sequentially onto 5-, 2-, and 0.2- $\mu\text{m}$  polycarbonate membranes. When more than one measurement was made within the mixing layer, the depth-weighted average was calculated. The mixing layer was defined as the layer above the depth at which  $\sigma_t$  increased by 0.03  $\text{kg m}^{-3}$  or temperature dropped by 0.1°C from the surface values. Mixing layer depths were 7, 6, 6, and 2 m for days 14, 15, 16, and 17 June, respectively.

Microzooplankton herbivory was determined by the dilution method (Landry and Hassett 1982; Archer et al. 2001). Water was collected predawn from a depth of 4 m, using 30-liter acid-cleaned Go-Flo bottles. Water was filtered through a Gelman 0.2- $\mu\text{m}$  pore-size capsule filter to produce the diluent. Prior to each experiment, filter capsules and silicon tubing were soaked in 10% HCl-Milli-Q water and rinsed with Milli-Q water, and the first several liters of filtered seawater discarded. Unfiltered water was gently passed through a 200- $\mu\text{m}$  gauze on addition to each incubation bottle. Twelve 2.3-liter polycarbonate bottles were used to allow triplicate incubations at four levels of dilution. All incubations were carried out in the same flow-through on-deck incubator flushed with seawater and covered with an acrylic screen and two sheets of Perspex in order to simulate a 55% PAR (400–700 nm) light level. The net rate of growth of the total phytoplankton population in each bottle was determined fluorometrically by changes in initial and final concentrations of Chl *a* measured in 90% acetone extracts of GF/F filtered water.

Bacterial production was determined with the tritiated leucine method (see Pedrós-Alió et al. 1999 for details). Aliquots of seawater collected before dawn from the surface were spiked with <sup>3</sup>H-leucine to a final concentration of 40 nM and incubated in the dark at near the in situ temperature (12°C) for 2 h. Bacterial heterotrophic production was calculated by applying an empirical conversion factor obtained from the mean of six experiments during the cruise (0.39  $\pm$  0.10  $\text{kgC biomass produced mol}^{-1}$  leucine incorporated).

Many authors do not perform experimental determinations of the “local” conversion factor, but rather take a reference value from the literature (generally 3.1 kgC mol<sup>-1</sup> leucine, Simon and Azam 1989). A number of studies where the conversion factor has been measured in open-ocean waters show that it can, however, be much lower than that reference value (e.g., Ducklow et al. 1993; see Pedrós-Alió et al. 1999 for discussion). We also performed thymidine incorporation experiments, which gave production results within 20% of those obtained with leucine. Leucine values were judged to be more appropriate for the purpose of the budget calculations.

To measure primary production in the on-deck 24-h incubation experiment, the photosynthetic characteristics ( $P_{\max}$  and  $\alpha$ ) were determined every 4 h from short-term <sup>14</sup>C incubations in a 24 irradiance photosynthetron. These parameters were used to estimate the time course of primary production in conjunction with the ambient irradiance, attenuation, and Chl *a* data.

**DMSP and DMS concentrations and fluxes**—DMS concentrations were measured by purge and trap gas chromatography from 25-ml aliquots of seawater filtered through Whatman GF/F glass fiber filters (nominal pore size: 0.7  $\mu$ m). Total (particulate + dissolved) DMSP was determined as DMS after alkaline hydrolysis of unfiltered samples and subtraction of the DMS concentration (Simó et al. 2000). On 13, 14, and 15 June, DMSP was determined in size-fractionated particles. This was achieved by gravitational filtration through a 10- $\mu$ m pore-size polycarbonate filter. The filtrate was further filtered through a GF/F filter that upon analysis provided the concentration of DMSP in particles <10  $\mu$ m. Filtration of whole seawater through GF/F provided whole particulate DMSP. Comparison of both provided the fraction of DMSP<sub>p</sub> occurring in particles more or less than 10  $\mu$ m.

DMSP consumption rates were determined by applying the net-loss curve approach (exponential decrease in total DMSP in dark incubations of whole seawater), with the assumption that no DMSP was synthesized de novo by organisms during the dark incubation period (Simó and Pedrós-Alió 1999a; Simó et al. 2000). DMSP production rates were estimated by balancing daily DMSP concentrations and consumption rates during the Lagrangian time series. The same methods were used to determine DMSP consumption and production rates in the on-deck 24-h incubation experiment, albeit every 4 h instead of daily. In both cases, DMSP production between sampling times  $t_i$  and  $t_{i+1}$  (DMSPprod <sub>$t_i \rightarrow t_{i+1}$</sub> ) was calculated by subtracting concentration changes predicted by initial concentrations and consumption rate (DMSPcons <sub>$t_i$</sub> ) from changes in in situ concentrations, as follows (Simó and Pedrós-Alió 1999a):

$$\begin{aligned} \text{DMSPprod}_{t_i \rightarrow t_{i+1}} &= \{[\text{DMSP}]_{t_{i+1}} - ([\text{DMSP}]_{t_i} - \text{DMSPcons}_{t_i} \cdot (t_{i+1} - t_i))\} \\ &\div (t_{i+1} - t_i). \end{aligned}$$

The rates of DMS loss through abiotic processes (air-sea exchange and photolysis) were taken from those estimated

for the corresponding dates by Simó and Pedrós-Alió (1999a).

The amount of dissolved DMSP + DMS released during grazing was calculated from microzooplankton biomass-specific DMSP + DMS release rates, determined in nearby waters using a modification of the dilution approach (Archer et al. 2001).

## Results and discussion

**Carbon and sulfur fluxes through phytoplankton**—Between 14 and 17 June, the phytoplankton assemblage in the labeled water patch was dominated by the species *E. huxleyi* (1,900–3,200 cell ml<sup>-1</sup>). Surface Chl *a* concentrations were 0.7–0.8  $\mu$ g L<sup>-1</sup>, of which 75% were in the >2- $\mu$ m size fraction. This gives an approximate biomass of phytoplankton >2  $\mu$ m of 27  $\mu$ gC L<sup>-1</sup> (2250 nmol C L<sup>-1</sup>). To determine the sulfur content of this phytoplankton >2  $\mu$ m, we applied a C/S (mol:mol) ratio of 50, which has been reported for exponentially growing cultures of *E. huxleyi* and other strong DMSP producers (Matrai and Keller 1994). The resulting particulate sulfur concentration in phytoplankton biomass was 45 nmol S L<sup>-1</sup>. DMS and total (particulate + dissolved) DMSP concentrations ranged between 3 and 5 nM and 37 and 49 nM, respectively. Particulate DMSP occurred at 29–31 nM, and DMSP<sub>p</sub>/Chl *a* ratios were 44–100 nmol  $\mu$ g<sup>-1</sup>. More than 75% of DMSP<sub>p</sub> was associated with algae in the 2–10- $\mu$ m size fraction. The contribution of DMSP carbon and DMSP sulfur to phytoplankton (>2  $\mu$ m) cellular carbon and sulfur was estimated considering that 1 mole of DMSP contains 5 moles of carbon and 1 mole of sulfur. According to this, DMSP represented on average 7% and 71% of algal carbon and sulfur content, respectively (Table 1). The contribution to carbon content is well within the range estimated by Kiene et al. (2000) through a compilation from the literature (0.2–39%, generally 1–10% in open-ocean surface waters). Matrai and Keller (1994) reported that DMSP was 9% of particulate organic carbon in cultured *E. huxleyi* and it exceeded 10% of the carbon content in cultures of other high-DMSP-producing algae. According to these same authors, DMSP can account for the majority of the particulate organic sulfur (50–100%) in some algae, 50% in cultured *E. huxleyi*. This agrees reasonably well with our estimate of 71% of algal sulfur in the form of DMSP. Ours and previous estimates illustrate that this single compound can comprise as high a proportion of the algal sulfur as all the other sulfur components (S-amino acids, sulfolipids, etc.) combined. This highlights the importance of DMSP in algal cell physiology and, particularly, in sulfur metabolism (Stefels 2000). Matrai and Keller (1994) observed that DMSP producers had higher levels of organic sulfur per unit cell volume.

DMSP production (biosynthesis) molar rates were multiplied by 5 to convert them into carbon units. Thus, this DMSP-C production could be compared with primary production. Figure 1a illustrates the relationship between diel primary production and DMSP production in surface waters of the eddy (including measurements made beyond the 4-d period). The significant ( $p < 0.005$ ) linear relationship ( $r = 0.95$ , slope = 0.07) indicates that DMSP biosynthesis was

Table 1. DMSP and the carbon and sulfur pools and fluxes in phytoplankton.

Date	Pools					Fluxes			
	DMSP <sub>p</sub> * (nmol S L <sup>-1</sup> )	Chl <i>a</i> concentration in particles >2 μm (μg L <sup>-1</sup> )	Fraction of total Chl <i>a</i> (%)	DMSP-C/ algal POC† (%)	DMSP-S/ algal POS‡ (%)	DMSP production§ (nmol S L <sup>-1</sup> )	Primary production >2 μm (nmol C L <sup>-1</sup> d <sup>-1</sup> )	Fraction of total primary production (%)	DMSP-C prod./ primary production >2 μm   (%)
14 June 98	29.0	0.63	74	6	55	17.3	1152	81	7
15 June 98	29.7	0.58	78	6	61	15.2	1168	81	7
16 June 98	30.0	0.57	81	6	63	24.4	1575	80	8
17 June 98	31.4	0.36	68	10	105	26.9	1405	82	10
Average (SD)	30.0 (1.0)	0.54 (0.12)	75 (6)	7 (2)	71 (23)	21.0 (5.6)	1325 (203)	81 (1)	8 (1)

\* Particulate (GF/F-retained) DMSP.

† Contribution of DMSP-carbon to particulate organic carbon in algae >2 μm, assuming a carbon/Chl *a* ratio of 50.

‡ Contribution of DMSP-sulfur to particulate organic sulfur in algae >2 μm, assuming a carbon/sulfur ratio of 50.

§ DMSP production rate = DMSP biosynthesis in algae.

|| Contribution of DMSP-carbon production to total carbon fixation through primary production in algae >2 μm.

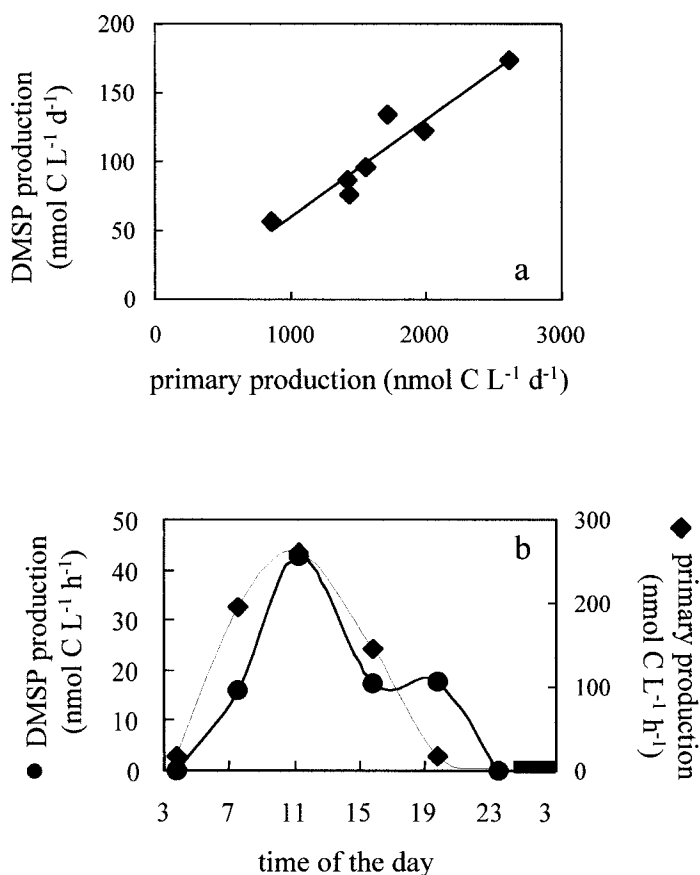


Fig. 1. Coupling between DMSP biosynthesis and primary production. (a) Diel DMSP production by phytoplankton versus diel primary production (both in carbon units) in waters sampled between 14 June and 3 July 1998. DMSP production rates were estimated in surface waters. Primary production rates are mixing layer averages. (b) Time course of hourly DMSP production and primary production rates (both in carbon units) in an on-deck microcosm experiment with surface water incubated under 50% natural light over 24 h on 3 July 1998. The black bar indicates the dark period.

proportional to photosynthesis and that phototrophs invested 7% of the total carbon fixed through net primary production in DMSP production. During the 4-d Lagrangian period, assuming that most new DMSP was produced by phytoplankton >2 μm (Keller et al. 1989; Corn et al. 1996), then 7–10% of carbon fixation by these organisms went into DMSP biosynthesis (Table 1). The <sup>14</sup>C technique used is thought to provide values closer to net primary production than to gross production; likewise, the method for estimating DMSP production rates might also provide slight underestimates of gross DMSP production, as the assumption is made that no DMSP at all is produced in the dark (Simó et al. 2000). Consequently, the combination of both effects makes us believe that the observed fraction of fixed carbon going into DMSP biosynthesis is not a large overestimate. Interestingly, the 7–10% (average 8%) obtained is in excellent agreement with our estimate of a mean 7% contribution of DMSP to phytoplankton carbon content (*see above*). It is worth highlighting the consistency between the results of two completely independent approaches to the contribution of DMSP to phytoplankton carbon: one approach uses measurements of Chl *a* and particulate DMSP pools and combines them through conversion factors, while the other uses measurements of carbon and DMSP production in incubations. This consistency adds support to the robustness of the procedures and assumptions used and the data obtained.

Further evidence for the coupling between photosynthesis and DMSP production was obtained from the 24-h deck-incubation experiment (Fig. 1b) carried out with water from the edge of the eddy. Dinoflagellates, small flagellates, and picophototrophs dominated the phytoplankton assemblage, with a DMSP to Chl *a* ratio of 94 nmol μg<sup>-1</sup>, i.e., at the upper end of the range found in the neighboring *E. huxleyi* bloom. Both DMSP biosynthesis and primary production exhibited a diel pattern peaking around noon.

Figures 1a and 1b together provide strong evidence that DMSP production in unicellular algae is a diurnal process proportional to photosynthesis. Although dark uptake of ex-

Table 2. DMSP and the carbon and sulfur fluxes through microzooplankton.

Date	Microzooplankton					
	DMSP ingested (nmol S L <sup>-1</sup> d <sup>-1</sup> )	DMSP-S released through grazing (nmol S L <sup>-1</sup> d <sup>-1</sup> )	DMSP-S assimilated by microzooplankton* (nmol S L <sup>-1</sup> d <sup>-1</sup> )	Microzooplankton net production† (nmol C L <sup>-1</sup> d <sup>-1</sup> )	DMSP-C assimilated/net production (%)	DMSP-S assimilated/S demand‡ (%)
14 June 98	9.8	6.6	3.2	328	5	49
15 June 98	10.0	6.7	3.3	398	4	41
16 June 98	13.4	9.0	4.4	490	5	45
17 June 98	20.0	13.4	6.6	588	6	56
Average (SD)	13.3 (4.8)	8.9 (3.2)	4.4 (1.6)	451 (113)	5 (1)	48 (6)

\* This is an upper limit, since the assumption is made that all DMSP not released as DMSP or DMS is assimilated by the grazer.

† Net production calculated from the daily increment in biomass.

‡ Contribution of DMSP-S assimilation (=incorporation into biomass) to microzooplankton sulfur demand, applying a C/S ratio of 50 to carbon production.

ogenous sulfate for amino acid synthesis has been observed in microalgae (e.g., Cuhel et al. 1984), the only evidence that the production of DMSP from methionine takes place in dark conditions has been reported by Stefels et al. (1996) for a culture of *Phaeocystis* sp. Our field results are consistent with indications that some of the enzymes involved in DMSP biosynthesis in *E. huxleyi* are closely linked to photosynthetic reactions and that the last steps of the synthesis pathway occur in the chloroplast (D. Gage, pers. comm.).

*Carbon and sulfur fluxes through microzooplankton*—Microzooplankton biomass increased from 1,493 nM carbon on day 14 to 2,928 nM on day 17, largely due to an increase in the biomass of oligotrichous ciliates, equivalent to a net doubling per day. The sulfur demand of microzooplankton was estimated by applying a carbon/sulfur (mol:mol) ratio of 50 to microzooplankton production. As we are not aware of any reported determination of the elemental composition of microzooplankton, we used this ratio, which is similar to that of high DMSP-producing phytoplankters in late exponential growth (Matrai and Keller 1994). Given the uncertainties in microzooplankton sulfur content, the use of a C:S ratio that is possibly too low results in a tendency to overestimate sulfur demand and underplay the importance of DMSP in meeting that demand.

Estimates of the DMSP<sub>p</sub> ingested by microzooplankton were calculated from the proportion of primary production >2 μm consumed (71%), determined by the dilution method, and the proportion of carbon production (>2 μm) channeled through DMSP<sub>p</sub> synthesis (average 7%, see above). The amount of dissolved DMSP + DMS released during grazing was calculated from microzooplankton biomass using microzooplankton biomass-specific DMSP + DMS release rates, determined in nearby waters by a modification of the dilution approach (Archer et al. 2001). Microzooplankton ingested between 10 and 20 nM (mean 13 nM) of algal DMSP per day and, of this, 67% (9 nM d<sup>-1</sup>) was released as dissolved DMSP + DMS (Table 2). This represented a transformation of 30% of the particulate DMSP stock to the dissolved phase per day. These values are in agreement with previous estimates made using single prey and predator marine isolates in laboratory cultures (Wolfe et

al. 1994; Christaki et al. 1996). With the assumption that all DMSP not released as DMSP + DMS is assimilated by the micrograzers, then DMSP assimilation contributed about 5% of carbon and 50% of sulfur to net microzooplankton production (Table 2). We have no direct evidence that all the nonreleased DMSP was assimilated. It might be that some was converted into dissolved compounds other than DMSP or DMS—such as methanethiol, dimethyl sulfoxide, or sulfate—right upon grazing, but with current knowledge there is no indication that such transformations can occur in the protozoan cell bodies unless through the action of associated bacteria. We also may be overestimating the DMSP contribution to carbon and sulfur demands of the microzooplankton if their gross production rates are considerably higher than the observed net rates. However, the net production rates observed for the oligotrich ciliates equaled to approximately one doubling per day, suggesting that they experienced a low rate of mortality.

*Carbon and sulfur fluxes through heterotrophic bacterioplankton*—Bacterial heterotrophic production was converted into sulfur demand using a bacterial carbon/sulfur (mol:mol) ratio of 86 found in bacteria associated with a bloom of DMSP-producing algae (Fagerbakke et al. 1996). Carbon demand was estimated using a bacterial growth efficiency (BGE) between 0.05 and 0.1. This low BGE stands well as a conservative but realistic lower limit because (a) it agrees with that estimated in a nearby area at a similar time of year (Kirchman et al. 1991; Kirchman 1994) and (b) it is obtained by applying to our production values (mean bacterial production: 51 nmol C L<sup>-1</sup> d<sup>-1</sup>; mean primary production: 1,640 nmol C L<sup>-1</sup> d<sup>-1</sup>) general empirical relationships between bacterial production or primary production and BGE (del Giorgio and Cole 1998, 2000).

The microbiota turned over total DMSP at a rate of 14–16 nM d<sup>-1</sup>. We can assume that all the sulfur and carbon contained in DMSP are eventually processed by bacteria (either as DMSP, DMS, acrylate, methanethiol, or any other product of DMSP degradation), except that portion made unavailable to microbes through abiotic processes, such as sea–air exchange and photochemical oxidation of DMS (Kieber et al. 1996; Simó and Pedrós-Alió 1999a). We sub-

Table 3. DMSP and the carbon and sulfur fluxes through heterotrophic bacteria.

Date	Bacteria					
	Total DMSP loss* (nmol S L <sup>-1</sup> d <sup>-1</sup> )	DMS abiotic loss rate† (nmol S L <sup>-1</sup> d <sup>-1</sup> )	DMSP-S bacterial consumption‡ (nmol S L <sup>-1</sup> d <sup>-1</sup> )	Bacterial heterotrophic production (nmol C L <sup>-1</sup> d <sup>-1</sup> )	DMSP-C consumed/ bacterial C demand§ (%)	DMSP-S assimilated/ bacterial S demand   (%)
14 June 98	16.4	5.3	11.1	24	15–30	395
15 June 98	14.4	8.8	5.6	65	4–8	73
16 June 98	14.4	9.7	4.7	78	3–6	51
17 June 98	14.4	5.7	8.7	36	8–16	210
Average (SD)	14.9 (1.0)	7.4 (2.2)	7.5 (2.9)	51 (25)	8–15 (5–11)	182 (158)

\* Loss of total DMSP in dark incubations = biological transformation of DMSP.

† Sum of DMS losses through air-sea exchange and photo-oxidation.

‡ Sulfur in DMSP and derivatives that is used by bacteria = total DMSP losses – abiotic DMS losses.

§ Contribution of DMSP-carbon consumed by bacteria to bacterial total carbon demand, applying growth efficiencies of 0.05–0.1 to bacterial heterotrophic production.

|| Contribution of DMSP-S assimilated (=DMSP-sulfur used by bacteria) to bacterial sulfur demand, applying a C/S ratio of 86 to bacterial heterotrophic carbon production and assuming that only 10% of the DMSP-sulfur used is incorporated into biomass.

tracted the measured rates of these two abiotic loss processes from DMSP consumption rates to compare microbial DMSP consumption with the carbon demand of heterotrophic bacteria (Table 3). With the conservative bacterial growth efficiency (0.05–0.1), DMSP and derivatives supported 8–15% of bacterial carbon demand. Similar numbers have been obtained for DMSP<sub>d</sub> by Kiene and Linn (2000a) in the Gulf of Mexico and by Zubkov et al. (2001) in a similar coccolithophore bloom in the northern North Sea. Also, these rates are comparable to those of important and ubiquitous metabolites such as glucose or amino acids in oligotrophic and mesotrophic open-ocean waters (Rich et al. 1996; Keil and Kirchman 1999).

It has been shown recently that DMSP acts as a precursor of protein sulfur in marine microbes and can potentially be a major source of sulfur to bacteria through assimilation of the S-moiety into biomass (Kiene et al. 1999). In our study, even if only a small fraction (10% as a very conservative estimate; Kiene and Linn 2000b; Kiene et al. 2000) of the DMSP sulfur used by bacteria were incorporated into bio-

mass, the DMSP flux to bacteria would be enough to potentially satisfy most of their sulfur demand for biomass production (Table 3). This is in good agreement both with Zubkov et al. (2001), who found that DMSP<sub>d</sub> contributed >50% of the sulfur flux through bacteria in the North Sea, and with Kiene and Linn (2000a), who found that DMSP-S assimilation satisfied 100% of the bacterial sulfur demand in the oligotrophic Gulf of Mexico.

*Contribution of DMSP and derivatives to food-web fluxes*—Figure 2 shows an integrated view of the food-web carbon fluxes to which DMSP and derivatives made up a significant contribution. Simple budget calculations were used to constrain the estimates of the fluxes that were not measured experimentally, such as dissolved organic carbon (DOC) release by phytoplankton and microzooplankton. Thus, phytoplankton release of DMSP and DOC not related to grazing (i.e., through autolysis, viral lysis, and exudation) was estimated by balancing the carbon fluxes: release by phytoplankton = production by photosynthesis – grazed production (there was no biomass accumulation: total Chl *a* concentrations decreased from 0.85 to 0.67 μg L<sup>-1</sup> within the 4 d). This result sets the upper limit of algal release of DMSP and DOC, since some primary production was probably lost through mesozooplankton grazing and sedimentation, and part of the algal carbon release was in the form of detrital particulate organic carbon (POC). A similar method was used to constrain total carbon release during microzooplankton grazing by approaching the problem from two perspectives: (a) release by microzooplankton = phytoplankton production grazed – microzooplankton production (710 nmol C L<sup>-1</sup> d<sup>-1</sup>; this sets the upper limit, since some microzooplankton production is lost by respiration, sedimentation, POC release, and mesozooplankton grazing); (b) release by microzooplankton = bacterial consumption – release by phytoplankton (45–540 nmol C L<sup>-1</sup> d<sup>-1</sup>; this sets the lower limit, since algal release is an upper limit and DOC losses other than bacterial are ignored). In budgeting for (b), if we use the lower limit of bacterial carbon consumption inferred

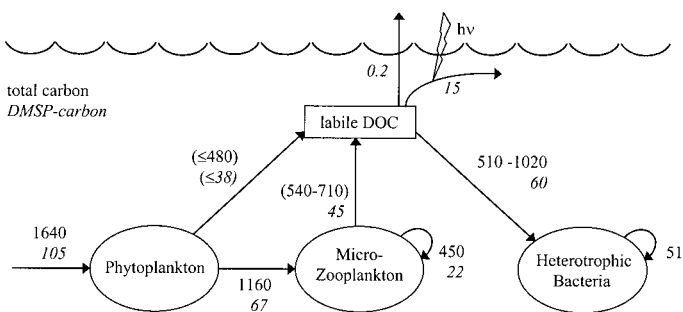


Fig. 2. DMSP and carbon cycling. Arrows represent fluxes (in nmol C L<sup>-1</sup> d<sup>-1</sup>) of total carbon (normal case) and carbon in the form of DMSP and derivatives (italics). Values are mixing layer measurements averaged for samples collected in Lagrangian mode on 14–17 June 1998. When data were not available the fluxes were estimated (numbers in parentheses) by balancing source and loss terms. Mixing layer depths were <10 m.

from the upper limit of bacterial growth efficiency of 0.1, i.e.,  $510 \text{ nmol C L}^{-1} \text{ d}^{-1}$ , then the total carbon released by microzooplankton equaled the carbon released as DMSP ( $45 \text{ nmol C L}^{-1} \text{ d}^{-1}$ ). It is materially impossible that all carbon was released as DMSP; therefore, either DOC accumulated or became refractory due to the effects of UV, or the bacterial growth efficiency was clearly lower than 0.1, i.e., closer to the suggested lower limit 0.05. With this lower growth efficiency, bacterial carbon consumption was  $1,020 \text{ nmol C L}^{-1} \text{ d}^{-1}$ , and the carbon release by microzooplankton through equation (b) amounted to  $540 \text{ nmol C L}^{-1} \text{ d}^{-1}$ . Therefore, we estimate that the DOC release by microzooplankton was most probably confined between 710 (a) and  $540 \text{ nmol C L}^{-1} \text{ d}^{-1}$  (b) (Fig. 2). The relative magnitudes of the carbon fluxes obtained are in agreement with the current view of carbon flow-through open-ocean microbial food webs (Nagata 2000). A large fraction of daily primary production (and associated DMSP) was grazed by microzooplankton, which were the main agents for the transformation of both carbon and DMSP from phytoplankton into the dissolved pool. Some 6–8% of the total carbon released by microzooplankton during grazing was in the form of DMSP and derivatives. These were lost from the surface waters mostly through bacterial metabolism, whereas DMS photochemical and ventilation losses (in this order) were of less importance.

Uncertainties are associated with the fluxes given in Tables 1–3 and Fig. 2, owing to the assumptions surrounding variables such as intracellular stoichiometric ratios, respiration, and assimilation rates, which were not directly quantified. However, the most realistic literature values were selected or, alternatively, lower limit values were used to yield conservative estimates of the desired fluxes. Therefore, the contributions of DMSP to carbon and sulfur fluxes are unlikely to be overestimated.

*Biogeochemical and ecological implications*—It is worth stressing that DMSP carbon contributed between 5 and 15% of all carbon fluxes (Tables 1–3 and Fig. 2), indicating that DMSP contributes as much to the microbial food-web fluxes as the most reactive components of labile dissolved organic matter (DOM) studied so far. Various authors (e.g., Rich et al. 1996; Keil and Kirchman 1999; Nagata 2000; and refs. therein) have observed that single DOM components such as glucose, amino acids, or DNA, although occurring in oceanic waters at nanomolar concentrations, turn over at high rates, thereby fuelling large fractions of carbon (and nitrogen or phosphorus) demands and recycling fluxes through the microbiota. Therefore, the study of cycling rates and pathways of these single labile substances (much easier to undertake and interpret than for total DOM) is of great utility in learning about DOM cycling and element recycling. Our results provide a solid basis for adding DMSP and derivatives to the list of major DOM-flux components.

Our findings are of particular importance for the study of organic sulfur (OS) dynamics in the surface ocean. Knowledge of OS as a component of the oceanic sulfur cycle is very poor. Particularly, little is known about the size of the dissolved (DOS) pool (Cutter and Dryden 1999) and even less about the routes and rates of its cycling. Because of the abundance of sulfate in seawater, its assimilation into organic

matter by phytoplankton is thought to represent the main supply of sulfur to the base of the food web. We have shown that DMSP is synthesized during photosynthesis (Fig. 1) and is, therefore, likely to be a major product of algal sulfate assimilation. Bacteria also assimilate dissolved sulfate, but they may benefit energetically from using dissolved DMSP and derivatives as a direct source of reduced sulfur for methionine synthesis (Kiene et al. 1999). Likewise, micrograzers apparently assimilate part of the DMSP present in their diet, thereby potentially satisfying a large fraction of their sulfur demand (Table 2). Eventually, both at the short and mid term, microbial degradation of the S-moiety of DMSP into sulfate (Kiene and Linn 2000b) may constitute a major process of DOS removal. Hence, this compound probably represents the main carrier involved in sulfur cycling through the microbial plankton.

In recent years, DMSP has emerged as a fascinating compound with an increasing number of essential physiological and ecological functions being revealed. Besides being a precursor to DMS it is a compatible solute involved in osmoregulation and cryoprotection in algae and bacteria, it is a methyl donor in metabolic reactions (Kiene et al. 1996; Malin and Kirst 1997, and refs. therein), and a precursor of chemical cues used for chemosensory attraction or deterrence (Nevitt et al. 1995; Wolfe et al. 1997). In addition, it is a sulfur source for methionine synthesis in bacteria (Kiene et al. 1999, 2000) and an overflow mechanism for excess reduced sulfur and reducing power in algae under conditions of unbalanced growth (Stefels 2000). Now we add that DMSP also plays an important role in the transference and cycling of sulfur and carbon among trophic levels in microbial food webs.

A number of critical steps in the DMSP cycle determine the amounts of DMSP sulfur and carbon that are transformed into DMS and can be vented to the atmosphere. The fraction of fixed carbon invested in DMSP biosynthesis depends on the relative abundance of DMSP-producing algae among primary producers. In many regions of the open ocean, a high proportion of stronger DMSP producers (dinoflagellates and small haptophytes) coincides with stratified conditions in late spring and summer (Dacey et al. 1998; Simó and Pedrós-Alió 1999b; Uher et al. 2000) rather than with seasons of active surface mixing and highest primary production, usually dominated by diatoms, which produce less DMSP. In such mesotrophic or oligotrophic stratified waters, the fraction of primary production released as DMSP and/or DMS through microzooplankton grazing will increase as phytoplankton cells tend to be smaller and microzooplankton (protozoan-dominated) grazing pressure tends to exceed mesozooplankton (crustacean-dominated) grazing (Legendre and Le Fèvre 1991; Burkill et al. 1993; Nagata 2000). Under such conditions, a combination of low export of sinking particles due to the dominance of small algae and microzooplankton grazers (Legendre and Le Fèvre 1991) and reduced vertical mixing will ensure that a larger proportion of DMSP and DMS is available to bacteria in the upper waters. Alternative scenarios may be envisaged in coastal and shelf ecosystems characterized by mixed waters, larger sized organisms, and the classical food chain.

Ultimately, the proportion of DMS escaping from this cy-

cling to the atmosphere will depend mainly on the balance between the availability of DMSP on the one hand and sulfur and carbon demands of heterotrophs on the other (Simó and Pedrós-Alió 1999b; Kiene et al. 2000), with contributions from vertical export and photooxidation of DMS (Kieber et al. 1996; Simó and Pedrós-Alió 1999a). The availability of DMSP is a consequence of phytoplankton taxonomy, production, and loss through lysis or grazing, and, therefore, it is dependent upon community structure and dynamics. Likewise, sulfur and carbon demands of bacteria and grazers are constitutive parts of food-web dynamics.

For years, many researchers have been trying to explain the variability of DMS concentrations in the surface ocean through the variability of phytoplankton, but attempts to directly relate DMS to algal biomass (Chl *a* levels) or primary production on a large scale have failed (Kettle et al. 1999). Our comprehensive study adds to the mounting evidence (e.g., Belviso et al. 1990; Bates et al. 1994; Matrai and Vernet 1997; Kiene et al. 2000) that DMS is a food-web by-product whose whole cycle (from algal DMSP production to DMS consumption) is embedded in microbial trophodynamics, so much so that the keys to understanding and prognostic modeling of the net production of this climatically active compound, and its response to climate forcing, are to be found in food-web (rather than phytoplankton alone) dynamics and how they change in relation to physicochemical conditions.

## References

- ANDREAE, M. O., AND P. J. CRUTZEN. 1997. Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry. *Science* **276**: 1052–1058.
- ARCHER, S. D., C. E. STELFOX-WIDDICOMBE, P. H. BURKILL, AND G. MALIN. 2001. A dilution approach to quantify the production of dissolved dimethylsulfoniopropionate and dimethylsulfide due to microzooplankton herbivory. *Aquat. Microb. Ecol.* **23**: 131–145.
- BATES, T. S., AND OTHERS. 1994. The cycling of sulfur in surface seawater of the northeast Pacific. *J. Geophys. Res.* **99**: 7835–7843.
- BELVISO, S. AND OTHERS. 1990. Production of dimethylsulfonium propionate (DMSP) and dimethylsulfide (DMS) by a microbial food web. *Limnol. Oceanogr.* **35**: 1810–1821.
- BURKILL, P. H., E. S. EDWARDS, A. W. G. JOHN, AND M. A. SLEIGH. 1993. Microzooplankton and their herbivorous activity in the northeastern Atlantic Ocean. *Deep-Sea Res. II* **40**: 479–493.
- CHARLSON, R. J., J. E. LOVELOCK, M. O. ANDREAE, AND S. G. WARREN. 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature* **326**: 655–661.
- CHRISTAKI, U., S. BELVISO, J. R. DOLAN, AND M. CORN. 1996. Assessment of the role of copepods and ciliates in the release to solution of particulate DMSP. *Mar. Ecol. Prog. Ser.* **141**: 119–127.
- CORN, M., S. BELVISO, F. PARTENSKY, N. SIMON, AND U. CHRISTAKI. 1996. Origin and importance of picoplanktonic DMSP, p. 191–202. *In* R. P. Kiene et al. [eds.], *Biological and environmental chemistry of DMSP and related sulfonium compounds*. Plenum.
- CUHEL, R. L., P. B. ORTNER, AND D. R. S. LEAN. 1984. Night synthesis of protein by algae. *Limnol. Oceanogr.* **29**: 731–744.
- CUTTER, G. A., AND C. L. DRYDEN. 1999. Dissolved organic sulfur in the Chesapeake Bay and western north Atlantic ocean, p. 52. *In* *Limnology and oceanography: Navigating into the next century*. Abstract Book, ASLO.
- DACEY, J. W. H., F. A. HOWSE, A. F. MICHAELS, AND S. G. WAKEHAM. 1998. Temporal variability of dimethylsulfoniopropionate in the Sargasso Sea. *Deep-Sea Res.* **45**: 2085–2104.
- DEL GIORGIO, P. A., AND J. J. COLE. 1998. Bacterial growth efficiency in natural aquatic systems. *Annu. Rev. Ecol. Syst.* **29**: 503–541.
- , AND ———. 2000. Bacterial energetics and growth efficiency, p. 289–326. *In* D. L. Kirchman [ed.], *Microbial ecology of the oceans*. Wiley.
- DUCKLOW, H. W., D. L. KIRCHMAN, H. L. QUINBY, C. A. CARLSON, AND H. G. DAM. 1993. Stocks and dynamics of bacterioplankton carbon during the spring bloom in the eastern North Atlantic Ocean. *Deep-Sea Res.* **40**: 245–263.
- FAGERBAKKE, K. M., M. HELDAL, AND S. NORLAND. 1996. Content of carbon, nitrogen, oxygen, sulfur and phosphorus in native aquatic and cultured bacteria. *Aquat. Microb. Ecol.* **10**: 15–27.
- KEIL, R. G., AND D. L. KIRCHMAN. 1999. Utilization of dissolved protein and amino acids in the northern Sargasso Sea. *Aquat. Microb. Ecol.* **18**: 293–300.
- KELLER, M. D., W. K. BELLOWS, AND R. R. L. GUILLARD. 1989. Dimethyl sulfide production in marine phytoplankton, p. 167–182. *In* E. Saltzman and W. J. Cooper [eds.], *Biogenic sulphur in the environment*. American Chemical Society.
- KETTLE, A. J., AND OTHERS. 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. *Glob. Biogeochem. Cycles* **13**: 399–444.
- KIEBER, D. J., J. JIAO, R. P. KIENE, AND T. S. BATES. 1996. Impact of dimethylsulfide photochemistry on methyl sulfur cycling in the equatorial Pacific Ocean. *J. Geophys. Res.* **101**: 3715–3722.
- KIENE, R. P., AND L. J. LINN. 2000a. Distribution and turnover of dissolved DMSP and its relationship with bacterial production and dimethylsulfide in the Gulf of Mexico. *Limnol. Oceanogr.* **45**: 849–861.
- , AND ———. 2000b. The fate of dissolved dimethylsulfoniopropionate (DMSP) in seawater: Tracer studies using <sup>35</sup>S-DMSP. *Geochim. Cosmochim. Acta* **64**: 2797–2810.
- , ———, AND J. A. BRUTON. 2000. New and important roles for DMSP in marine microbial communities. *J. Sea Res.* **43**: 209–224.
- , ———, J. GONZALEZ, M. A. MORAN, AND J. BRUTON. 1999. Dimethylsulfoniopropionate and methanethiol are important precursors of methionine and protein-sulfur in marine bacterioplankton. *Appl. Environ. Microbiol.* **65**: 4549–4558.
- , P. T. VISSCHER, M. D. KELLER, AND G. O. KIRST [EDS.]. 1996. *Biological and environmental chemistry of DMSP and related sulfonium compounds*. Plenum.
- KIRCHMAN, D. L. 1994. The uptake of inorganic nutrients by heterotrophic bacteria. *Microb. Ecol.* **28**: 255–271.
- , Y. SUZUKI, C. GARSIDE, AND H. W. DUCKLOW. 1991. High turnover rates of dissolved organic carbon during a spring phytoplankton bloom. *Nature* **352**: 612–614.
- LANDRY, M. R., AND R. P. HASSETT. 1982. Estimating the grazing impact of marine microzooplankton. *Mar. Biol.* **67**: 283–288.
- LEGENDRE, L., AND J. LE FÈVRE. 1991. From individual plankton cells to pelagic marine ecosystems and to global biogeochemical cycles, p. 261–300. *In* S. Demers [ed.], *Particle analysis in oceanography*. Springer.
- LESSARD, E. J. 1991. The trophic role of heterotrophic dinoflagellates in diverse marine environments. *Mar. Microb. Food Webs* **5**: 49–58.
- MALIN, G., AND G. O. KIRST. 1997. Algal production of dimethyl sulfide and its atmospheric role. *J. Phycol.* **33**: 889–896.



- MATRAI, P. A., AND M. D. KELLER. 1994. Total organic sulfur and dimethylsulfoniopropionate (DMSP) in marine phytoplankton: Intracellular variations. *Mar. Biol.* **119**: 61–68.
- , AND M. VERNET. 1997. Dynamics of the vernal bloom in the marginal ice zone of the Barents Sea: Dimethyl sulfide and dimethylsulfoniopropionate budgets. *J. Geophys. Res.* **102**: 22965–22979.
- NAGATA, T. 2000. Production mechanisms of dissolved organic matter, p. 121–152. *In* D. Kirchman [ed.], *Microbial ecology of the oceans*. Wiley.
- NEVITT, G. A., R. R. VEIT, AND P. M. KAREIVA. 1995. Dimethyl sulphide as a foraging cue for Antarctic Procellariiform seabirds. *Nature* **376**: 680–682.
- NIELSEN, M. V. 1997. Growth, dark respiration and photosynthetic parameters of the coccolithophorid *Emiliania huxleyi* (Prymnesiophyceae) acclimated to different day length-irradiance combinations. *J. Phycol.* **33**: 818–822.
- PEDRÓS-ALIÓ, C., J. I. CALDERÓN-PAZ, N. GUIXA-BOIXEREU, M. ESTRADA, AND J. M. GASOL. 1999. Bacterioplankton and phytoplankton biomass and production during summer stratification in the northwestern Mediterranean Sea. *Deep-Sea Res. I* **46**: 985–1019.
- PUTT, M., AND D. K. STOCKER. 1989. An experimentally determined carbon: volume ratio for marine 'oligotrichous' ciliates from estuarine and coastal waters. *Limnol. Oceanogr.* **34**: 1097–1103.
- RICH, J. H., H. W. DUCKLOW, AND D. L. KIRCHMAN. 1996. Concentrations and uptake of neutral monosaccharides along 140°W in the equatorial Pacific: Contribution of glucose to heterotrophic bacterial activity and the DOM flux. *Limnol. Oceanogr.* **41**: 595–604.
- SAVIDGE, G., AND L. GILPIN. 1999. Seasonal influences on size-fractionated chlorophyll *a* concentrations and primary production in the north-west Indian Ocean. *Deep-Sea Res. II* **46**: 701–723.
- SIMÓ, R. 2001. Production of atmospheric sulfur by oceanic plankton: Biogeochemical, ecological and evolutionary links. *Trends Ecol. Evol.* **16**: 287–294.
- , AND C. PEDRÓS-ALIÓ. 1999a. Short-term variability in the open ocean cycle of dimethylsulfide. *Glob. Biogeochem. Cycles* **13**: 1173–1181.
- , AND ———. 1999b. Role of vertical mixing in controlling the oceanic production of dimethyl sulphide. *Nature* **402**: 396–399.
- , G. MALIN, AND J. O. GRIMALT. 2000. Biological turnover of DMS, DMSP and DMSO in contrasting open-sea waters. *Mar. Ecol. Prog. Ser.* **203**: 1–11.
- SIMON, M., AND F. AZAM. 1989. Protein content and protein synthesis rates of planktonic marine bacteria. *Mar. Ecol. Prog. Ser.* **51**: 201–213.
- STEFELS, J. 2000. Physiological aspects of the production and conversion of DMSP in marine algae and higher plants. *J. Sea Res.* **43**: 183–197.
- , W. W. C. GIESKES, AND L. DIJKHUIZEN. 1996. Intriguing functionality of the production and conversion of DMSP in *Phaeocystis* sp, p. 305–315. *In* R. P. Kiene et al. [eds.], *Biological and environmental chemistry of DMSP and related sulfonium compounds*. Plenum.
- TANG, K. W., H. G. DAM, P. T. VISSCHER, AND T. D. FENN. 1999. Dimethylsulfonio-propionate (DMSP) in marine copepods and its relation with diets and salinity. *Mar. Ecol. Prog. Ser.* **179**: 71–79.
- UHER, G., G. SCHEBESKE, R. G. BARLOW, D. G. CUMMINGS, R. F. C. MANTOURA, S. R. RAPSOMANIKIS, AND M. O. ANDREAE. 2000. Distribution and air-sea gas exchange of dimethyl sulphide at the European western continental margin. *Mar. Chem.* **69**: 277–300.
- WOLFE, G. V., E. B. SHERR, AND B. F. SHERR. 1994. Release and consumption of DMSP from *Emiliania huxleyi* during grazing by *Oxyrrhis marina*. *Mar. Ecol. Prog. Ser.* **111**: 111–119.
- , M. STEINKE, AND G. O. KIRST. 1997. Grazing-activated chemical defence in a unicellular marine alga. *Nature* **387**: 894–897.
- ZUBKOV, M. V., B. M. FUCHS, S. D. ARCHER, R. P. KIENE, R. AMANN, AND P. H. BURKILL. 2001. Linking the composition of bacterioplankton to rapid turnover of dissolved dimethylsulfoniopropionate in an algal bloom in the North Sea. *Environ. Microbiol.* **3**: 304–311.

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