

Production and turnover of particulate dimethylsulphoniopropionate during a coccolithophore bloom in the northern North Sea

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ABSTRACT: Dimethylsulphoniopropionate (DMSP) synthesised by phytoplankton is the principal precursor of the climatically active gas dimethyl sulphide (DMS). The rates of production of particulate DMSP (DMSPp) and turnover by microzooplankton were determined in surface waters of the northern North Sea, using a dilution approach. The phytoplankton communities were characterised by DMSP-rich taxa including *Emiliana huxleyi* and *Prorocentrum minimum* and DMSPp:chlorophyll *a* (chl *a*) ratios of 64 to 162 nM μg^{-1} . Microzooplankton biomass varied from 25.5 to 56.7 $\mu\text{g C l}^{-1}$ and was dominated by oligotrich ciliates and heterotrophic dinoflagellates. DMSPp production rates ranged from 14.8 to 45.6 nM d^{-1} and represent a doubling time of the ambient DMSPp pool of between 1.2 and 3.1 d. Consumption rates of DMSPp by microzooplankton varied between 11.4 and 59.9 nM d^{-1} and were equivalent to turnover rates of the ambient DMSPp pool of between 16 and 43% d^{-1} . In general, production rates of DMSPp were lower than those of chl *a* and *E. huxleyi*, with respective mean doubling times of 1.9, 1.5 and 1.3 d. Loss rates due to grazing were similar for DMSPp and *E. huxleyi* but generally significantly lower than those of the bulk phytoplankton, with mean turnover rates of 31, 30 and 40% d^{-1} of the standing stock of DMSPp, *E. huxleyi* and chl *a*, respectively. *E. huxleyi* contributed an estimated 2 to 25% of the total DMSPp production and 6 to 23% of the DMSPp ingested by microzooplankton, indicating the importance of other phytoplankton to DMSPp dynamics in '*E. huxleyi* blooms'. At the depths sampled, DMSPp production was closely coupled to primary production and was equivalent to approximately 11% of the carbon fixation. DMSPp may be an important component of the diets of microzooplankton. Ingested DMSPp could have provided 2 to 3% of the microzooplankton carbon demand and 26 to 44% of their sulphur demand. DMSPp production and turnover rates were closely matched and suggest that in these waters microzooplankton grazing may be the principal determinant of the fate of DMSPp. The quantity of 'DMSP' excreted by microzooplankton, calculated from ingestion rates, biomass and assumed growth rates and growth efficiencies, ranged from 8.0 to 41.9 nM d^{-1} . This is equivalent to 13 to 35% d^{-1} of the DMSPp standing stocks and sufficient to support a daily turnover of the DMS plus dissolved DMSP (DMS+DMSPd) pool.

KEY WORDS: Dimethylsulphoniopropionate (DMSP) · Production rate · Grazing rate · *Emiliana huxleyi* · microzooplankton · Dimethyl sulphide (DMS) · North Sea

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INTRODUCTION

Dimethylsulphoniopropionate (DMSP) is an organic sulphur compound synthesised by marine micro- and macroalgae and a small number of higher plants. A

great deal of interest in DMSP stems from the fact that it is the principal precursor of dimethyl sulphide (DMS) in the oceans. Marine emissions of DMS amount to more than half the natural flux of sulphur to the atmosphere (Andreae & Crutzen 1997). Once in the atmosphere, DMS is oxidised to sulphuric acid and methanesulphonate, forming sub-micrometer particles that scatter solar radiation and may act as cloud condensa-

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tion nuclei affecting cloud radiative transfer and hence climate (Charlson et al. 1987, Ayers & Gras 1991). One of the keys to understanding the links between biogenic DMS production and climate is to discern the processes that control DMS concentrations in seawater (Liss et al. 1997). This is known to involve a multitude of interactive biological, chemical and physical processes. Of central importance is the rate at which phytoplankton produce DMSP and the fate of that production.

DMSP may make a substantial contribution to the organic sulphur (50 to 100%) and organic carbon content (>10%) of DMSP-rich micro-algae (Matrai & Keller 1994). Why phytoplankton produce DMSP is not entirely clear and several physiological roles have been suggested (reviewed in Stefels 2000). The most commonly held view is that DMSP, along with a number of other compounds, acts as a compatible solute in cells (Viaravamurthy et al. 1985, Dickson & Kirst 1987a,b, Kirst 1996). In a similar osmotic role, DMSP may act as a cryoprotectant, and high concentrations have been recorded in polar macroalgae (Karsten et al. 1992) and in sea-ice micro-algae (Kirst et al. 1991, Trevena et al. 2000). DMSP synthesis in marine micro-algae is thought to proceed via 1 of 3 elucidated pathways from methionine and involves transamination, reduction, S-methylation and oxidative decarboxylation steps (Gage et al. 1997). Stefels (2000) proposed that DMSP may be a by-product of the metabolic regulation of the sulphur containing amino acids cysteine and methionine. DMSP may be employed as a methyl donor in biological transmethylation reactions (Ishida 1996 and references therein) and may be a precursor in the biosynthesis of the membrane phospholipid phosphatidylsulphocholine in marine micro-algae (Kates & Volcani 1996). In addition, DMSP is thought to have a role as a grazing deterrent when ingestion or digestion of phytoplankton by grazers results in its enzymatic cleavage to DMS and acrylate (Wolfe & Steinke 1996). Perhaps because of this variety of roles, there is considerable interspecific variability in the intracellular concentrations of DMSP in phytoplankton (Keller et al. 1989). The distributions of particulate DMSP (DMSPp) in natural waters are thought to reflect these differences, with particularly high concentrations correlated with the abundance of the prymnesiophytes *Phaeocystis* sp. and *Emiliana huxleyi* and with a variety of dinoflagellates (e.g. Barnard et al. 1984, Holligan et al. 1987, Turner et al. 1988, 1996, Malin et al. 1993, Matrai & Keller 1993).

Predictive models of DMS emission have progressed from using a single DMSP:phytoplankton biomass quota to determine DMSP production rates (Gabric et al. 1993) to ascribing different DMSP quotas to differing components of the phytoplankton (van den Berg

1996) and, further, to using varying cell-specific DMSP synthesis rates in relation to the growth phase of the phytoplankton bloom (Laroche et al. 1999). Direct estimates of DMSPp production in natural waters are scarce. At a time series station in the northeastern Pacific, Bates et al. (1994) spiked water samples with $^{35}\text{SO}_4^{2-}$ and determined the incorporation rate of radiolabel into non-protein reduced sulphur, which would include DMSP-sulphur. During a Lagrangian experiment in the Iceland Basin, Simó & Pedrós-Alió (1999) were able to estimate a total (particulate+dissolved) DMSP production rate from measurements of DMSP consumption (calculated as the decrease in total DMSP in bottles incubated in the dark) and *in situ* net DMSP production between sampling dates.

Processes that typically control the fate of primary production also control the fate of DMSPp, including its transformation to dissolved DMSP (DMSPd) and DMS. Actively growing phytoplankton cells appear to excrete little DMS or DMSPd, and seawater concentrations of DMS are often poorly correlated to the biomass of phytoplankton (e.g. Leck et al. 1990, Dacey et al. 1998). However, enhanced DMSP exudation does result from phytoplankton senescence and has been linked to nutrient deficiency (Nguyen et al. 1988) and cell sedimentation (Osinga et al. 1996). Viral lysis of phytoplankton results in the release of DMSP in laboratory cultures (Hill et al. 1998, Malin et al. 1998), and viruses are known to affect the productivity of blooms of DMSP-rich *Emiliana huxleyi* in natural waters (Bratbak et al. 1996). Laboratory studies have shown that grazing by copepods on dinoflagellates and by protozoans on prymnesiophytes enhances DMS production (Dacey & Wakeham 1986, Malin et al. 1994, Christaki et al. 1996, Wolfe & Steinke 1996). In addition, several field studies have suggested that grazing is a key route by which DMSPd and DMS are produced (Belviso et al. 1990, Leck et al. 1990, Holligan et al. 1993, Christaki et al. 1996, Daly & DiTullio 1996). However, grazing does not always result in DMS or DMSPd production (Wolfe et al. 1994, Kwint et al. 1996), and a proportion of ingested DMSPp may be assimilated by grazers either directly into their tissue (Tang et al. 1999) or to meet carbon and sulphur demand. Microzooplankton are capable of consuming 20 to >100% of primary production each day (e.g. Gifford 1988, Burkill et al. 1993, Verity et al. 1996). Despite the potential importance of microzooplankton herbivory in determining the fate of phytoplankton DMSP and evidence that grazing transforms phytoplankton DMSP to DMS, direct estimates of the turnover of DMSPp by grazers in natural waters is limited.

One approach routinely used to estimate instantaneous growth rates of phytoplankton and turnover rates by microzooplankton is the dilution technique

(Landry & Hassett 1982). Generally, measurements of the changes in concentration of chlorophyll *a* (chl *a*) in a series of incubations diluted to varying degrees to create a gradient of grazing pressure yield an estimate of the growth and mortality of the phytoplankton community. Modifications of the method have evolved to examine growth and mortality rates of specific components of the phytoplankton by quantifying changes in specific pigments (e.g. Burkill et al. 1987, Strom & Welshmeyer 1991, Latasa et al. 1997) and by enumerating specific cell types (e.g. Landry et al. 1984, 1995b). In addition, the method has been used to examine rates of nitrogen uptake, regeneration and excretion (Andersen et al. 1991, Neuer & Franks 1993, Lehrter et al. 1999). Recently, the dilution approach has been applied to estimates of DMS+DMSP_d production rates due to microzooplankton grazing (Archer et al. 2001) and to examine grazing rates on DMS_P versus chl *a* in the Labrador Sea (Wolfe et al. 2000).

The specific aim of the present study was to determine a rate of production and turnover of DMS_P in surface waters containing DMS_P-rich phytoplankton. The approach taken involved combining dilution experiments with measurements of DMS_P. This allowed us to closely couple microzooplankton grazing with DMS_P production and turnover. On the basis of this information we address the contribution of DMS_P to grazer diets, assess the rate of transformation of DMS_P to DMS+DMSP_d by grazers and estimate the proportion of primary production invested in DMS_P synthesis by phytoplankton. We demonstrate that the dilution approach can provide new insights into the production and fate of DMS_P with implications for its transformation to DMS.

MATERIALS AND METHODS

The present study formed part of a multidisciplinary programme (dimethyl sulphide biogeochemistry within a coccolithophore bloom, DISCO) aboard the

RRS 'Discovery' in June 1999. A relatively small (~2000 km²), coherent bloom of *Emiliana huxleyi* was located by remote sensing of 555 nm backscatter and true colour images (SeaWiFS) in the Northern North Sea at approximately 58°56' N, 02°2' E. A 3 × 4 mile (4.8 × 6.4 km) patch of water at the southeastern edge of the bloom was labelled with sulphur hexafluoride (SF₆) to provide a Lagrangian component to the study (e.g. Law et al. 1998). Tracking and sampling of the SF₆ labelled waters (Nightingale et al. 2000) continued from 17 to 24 June. Subsequently, sampling was carried out at a variety of locations within the bloom. A dilution experiment was carried out each day in which the net changes in DMS_P, chl *a* and abundance of specific phytoplankton were monitored. To support this information, water samples were collected to provide a detailed description of the phytoplankton and microzooplankton communities present.

Experimental set-up. The approach used for dilution experiments was based on the protocol of Landry & Hassett (1982) and Landry et al. (1995a). The dates on which experiments were started and the location and environmental conditions of the sampled water are shown in Table 1. Initially, samples were collected from 5 m to coincide with the depth of maximum SF₆ concentration and to sample the surface mixed layer of approximately 20 m. However, the sampling depth was increased to 10 m after 23 June to account for subduction of the SF₆ labelled patch beneath a 4 to 5 m layer of less dense water originating to the east of the bloom. Water sampling took place pre-dawn using 30 l Niskin bottles with Teflon coated stainless steel springs. Prior to each experiment, filter capsules, silicon tubing and carboys were soaked in 10% HCl-Milli-Q water and rinsed with Milli-Q water; the first 5 to 10 l of filtered seawater was discarded. Seawater was gravity filtered through a 0.2 µm Gelman Criticap filter into 20 l carboys to produce 4 levels of dilution (20, 40, 70 and 100% ambient plankton densities). A second CTD cast was used to collect water from the same depth, and this was gently siphoned into each

Table 1. Position and environmental parameters of water sampled for dilution experiments. The sampling location relative to the SF₆-labelled patch and the 2000 km² *Emiliana huxleyi* bloom is also shown

Day in June	Position	Depth (m)	Temperature (°C)	Salinity (PSU)	Location
18	58° 52.6' N, 03° 03.0' E	5	11.6	35.007	Lagrangian patch
19	58° 49.5' N, 03° 12.8' E	5	11.6	35.041	Lagrangian patch
21	58° 36.8' N, 03° 30.9' E	5	11.3	35.002	Lagrangian patch
22	58° 30.8' N, 03° 30.4' E	5	11.5	34.817	Lagrangian patch
24	58° 20.5' N, 03° 28.4' E	10	11.2	35.030	SE edge of bloom
26	58° 15.2' N, 03° 33.7' E	11	11.2	35.085	SE edge of bloom
27	58° 46.8' N, 02° 40.1' E	11	11.6	35.135	Bloom centre
28	58° 42.0' N, 02° 30.6' E	11	12.3	34.998	S edge of bloom

carboy through a 200 µm mesh bag to remove mesozooplankton. The experimental water from each carboy was then siphoned into triplicate 2.3 l polycarbonate bottles and nutrients added to each bottle. Nitrate (NaNO_3), ammonium (NH_4Cl), phosphate ($\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$) and silicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) were added to produce a final concentration of added nutrients in each incubation bottle of 17.4 nM for the first 4 experiments. This was reduced to 8.7 nM for the final 4 experiments as nutrient levels decreased in the sampled waters. Three bottles containing undiluted water without nutrient enrichment were used as natural seawater controls. Incubations were carried out in a flow-through on-deck incubator for 24 h. Incubators were covered with a neutral density filter and 2 sheets of Perspex to simulate either 55% (5 m samples) or 33% (10 m samples) PAR (photosynthetically active radiation, 400 to 700 nm). Initial (T_0) concentrations of DMSPp, chl *a* and the abundance of *Emiliania huxleyi* were determined from triplicate subsamples taken from the 4 carboys. Final (T_{24}) concentrations were measured from each incubation bottle.

DMSP and DMS analyses. A cryogenic purge-and-trap/gas chromatography (GC) system similar to that described by Turner et al. (1990) was used to determine DMS concentrations. A Varian 3800 gas chromatograph equipped with a pulsed flame photometric detector (PFPD) was used to analyse all samples. The analytical column used was a 30 m × 0.53 mm CP Sil 5CB from Chrompack and was operated isothermally at 60°C. Nitrogen was the carrier gas at a flow rate of 5 ml min⁻¹. DMS standards for calibration were prepared from DMSP-HCl (>98% purity, CASS, University of Groningen) in Milli-Q water to which NaOH was added to a final concentration of 0.5 M.

For DMSPp analysis, samples of 15 ml from the carboys or incubation bottles were gravity filtered onto a GF/F filter. DMSPp was analysed as DMS following alkaline hydrolysis of filters in 22 ml sealed glass vials to which 0.5 M NaOH had been added. Subsamples of 1 to 5 ml from the sealed vials were purged for 5 to 10 min at 50 ml min⁻¹. Initial concentrations of DMS were determined in 10 ml of filtrate, which was immediately transferred to a purge chamber for analysis. The filtrate was sparged with nitrogen at 50 ml min⁻¹ for 12.5 min. The purged filtrate was used to determine DMSPd concentrations following hydrolysis with NaOH as for DMSPp samples. The purge gas was passed through a cold finger at 0°C followed by an ME Gas Dryer™ prior to entering a cryotrap consisting of a 1/16" (~1.6 mm) Teflon loop maintained at -160°C above liquid nitrogen. After purging, the trap was heated to 95°C to transfer the trapped gas to the GC system. The detection limit of the system for DMS was approximately 50 pg S. The precision (% SE) of tripli-

cate DMSPp and DMS measurements was typically 3.0 and 3.2%, respectively.

Chl *a* analysis. The initial and final concentrations of chl *a* were determined by filtration of samples of 100 to 500 ml onto 0.2 µm polycarbonate filters and fluorometric analysis of chl *a* extracted in 90% acetone at -20°C. The precision (% SE) of triplicate chl *a* measurements was typically ≤5.0%.

***Emiliania huxleyi* abundance.** The initial and final abundance of *E. huxleyi* was determined by analytical flow cytometry (AFC) of unfixed samples. AFC counts were performed with either a FACSort or FACScan flow cytometer (Becton Dickinson, Oxford, UK) equipped with 15 mW lasers exciting at 488 nm and with standard filter setups. Counts of quality control beads and nanophytoplankton on the 2 flow cytometers showed close agreement. Flow rates of the flow cytometers were calibrated routinely by measuring the changes in volume of samples run for differing lengths of time. Log measurements of side scatter (65 to 110°) and red (>650 nm) fluorescence were collected as list-mode data, and plots were produced and analysed using the WinMDI freeware (Joseph Trotter, The Scripps Research Institute [<http://facs.scripps.edu>]). The lithed cells of *E. huxleyi* were distinguished from other nanophytoplankton by their high side scatter signals compared to other cells with similar levels of red (chl *a*) fluorescence. Counts of over 250 cells were required to obtain estimates of *E. huxleyi* abundance of high enough precision (≤5% SE), requiring >15 min sample runs for the most dilute incubations at a flow rate of approximately 100 µl min⁻¹.

Determination of primary production. At each of 8 depths within the euphotic zone 8 × 60 ml polycarbonate bottles were filled with sea water and inoculated with 10 mCi $\text{NaH}^{14}\text{CO}_3$. Two of each set of 8 bottles were incubated in the dark; the remainder were incubated in a series of on-deck incubators at 97 to 1% of ambient irradiance and at surface seawater temperature. Incubations were terminated after 24 h by filtration. The phytoplankton population was divided into >5.0 and 5.0 to 0.2 µm by size fractionation onto appropriate polycarbonate filters. Filters were dried over silica gel prior to onboard counting of ¹⁴C activity using a scintillation counter to determine total carbon uptake rates. Counts were corrected for counting efficiency using an external standard, channels ratio method.

Characterisation of the plankton. A combination of AFC of unfixed samples and microscopy of fixed samples was employed to characterise the phytoplankton communities in waters sampled for the dilution experiments. Phytoplankton larger than approximately 10 µm were enumerated by inverted microscopy in 50 ml subsamples fixed in acid Lugol's (1% final concentration) and settled for >72 h. Linear dimensions of

each taxon were used to calculate cell volume based on appropriate geometric shapes and converted to carbon according to Kovala & Larrance (1966). Autotrophic cells smaller than approximately 10 μm were enumerated using AFC (see above) and cell size determined by size fractionation (Tarran et al. 2001).

Microzooplankton taxonomy, abundance and biovolume were determined in samples from the undiluted carboy used in the set-up of dilution experiments. Samples of 250 ml were fixed with acid Lugol's (1% final concentration). Between 20 and 50 ml subsamples were allowed to settle for ≥ 24 h, and all heterotrophic individuals smaller than 200 μm (excluding heterotrophic nanoflagellates < 20 μm) were identified and enumerated using an inverted microscope. The microzooplankton were sized using image analysis, and cell volumes were calculated assuming appropriate geometric shapes. The biovolume of each cell was then converted into carbon using conversion factors of 0.14 $\text{pg C } \mu\text{m}^{-3}$ for dinoflagellates (Lessard 1991) and 0.19 $\text{pg C } \mu\text{m}^{-3}$ for ciliates (Putt & Stoecker 1989). All ciliated protozoa were enumerated. Heterotrophic dinoflagellates were distinguished from autotrophic taxa according to Lessard & Swift (1986).

Data analyses. Apparent rates of change (k , d^{-1}) of DMSPp, chl a and *Emiliana huxleyi* were calculated from mean T_0 values at each level of dilution and T_{24} measurements from each incubation bottle, assuming an exponential model as described by Landry & Hassett (1982). Model I regression analysis (Sokal & Rohlf 1995) of the relationship between apparent rate of change and fraction of whole water was used to calculate estimates of instantaneous growth (μ , d^{-1}) and loss due to grazing (g , d^{-1}) for each of the 3 variables. The level of dilution (proportion of whole water in the dilution treatment) was calculated from initial concentrations of each variable relative to the concentration in unfiltered water.

RESULTS

Community composition, primary production and DMSPp

The initial concentrations of chl a , DMSPp and specific phytoplankton taxa in the waters used for dilution experiments are listed in Table 2. Chl a concentrations were relatively low and DMSPp concentrations high, giving DMSPp:chl a ratios of 64 to 162 $\text{nM } \mu\text{g}^{-1}$ (Table 2). Despite being the most obvious component of the phytoplankton community in surface water, *Emiliana huxleyi* abundance was moderate, ranging from 536 to 1092 $\times 10^3$ cells l^{-1} (Table 2). Another notable component was the autotrophic dinoflagellate *Prorocentrum minimum*, which occurred at concentrations of 0 to 221 $\times 10^3$ cells l^{-1} (Table 2). Other autotrophic nanophytoplankton (510 to 2660 $\times 10^3$ cells l^{-1}) and autotrophic picoeukaryotes (1260 to 15 100 $\times 10^3$ cells l^{-1}) were also a conspicuous component of the phytoplankton communities. In contrast, diatoms were relatively scarce and contributed only a minor proportion ($\leq 7\%$) of the phytoplankton biomass in surface waters.

Based on a value of 1.3 pg DMSP cell^{-1} (Keller et al. 1989, S.D.A. unpubl.), *Emiliana huxleyi* contributed 5 to 15% of the total DMSPp (Fig. 1). The population of *Prorocentrum minimum* was most abundant during the Lagrangian phase of the study but absent in the latter 2 experiments; it contributed an estimated 0 to 35% of the total DMSPp (Fig. 1), based on a cell-specific content of 21.4 pg DMSP cell^{-1} (Keller et al. 1989). Rough approximations of the DMSPp content of the other autotrophic dinoflagellates, nanophytoplankton and the autotrophic picoeukaryotes suggest that the source of almost 50% of the total DMSPp is undefined on some dates (Fig. 1).

Primary production determined as the rate of incorporation of ^{14}C in both >5 μm and 5 to 0.2 μm size frac-

Table 2. Biological and chemical characteristics of the water used in the dilution experiments. Shown are the initial concentrations of chlorophyll a (chl a), DMSPp, DMSPd, DMS, the abundance of the DMSP-rich phytoplankton *Emiliana huxleyi* and *Prorocentrum minimum*, microzooplankton (MZP) biomass and the abundance of the dominant ciliate taxon, provisionally identified as *Strombidium ovale*. Also included are estimates of primary production (^{14}C PP) measured in water sampled at the same depths and times as water used for the dilution experiments

Day in June	Chl a ($\mu\text{g l}^{-1}$)	^{14}C PP (nM C d^{-1})	DMSPp (nM)	DMS (nM)	DMSPd (nM)	DMSP:chl a ($\text{nM } \mu\text{g}^{-1}$)	<i>E. huxleyi</i> (10^3 cells l^{-1})	<i>P. minimum</i> (10^3 cells l^{-1})	MZP ($\mu\text{g C l}^{-1}$)	<i>S. ovale</i> -type (10^3 cells l^{-1})
18	0.40	1480	64	3.7	4.9	153 (± 9)	536	108	25.5	6.4
19	0.43	1990	54	3.9	4.4	131 (± 6)	657	118	28.1	4.0
21	0.91	2770	59	4.0	16.4	64 (± 3)	895	125	41.0	8.7
22	1.03	2510	68	4.6	9.3	70 (± 7)	1092	81	37.6	7.6
24	0.74	1690	121	5.2	8.4	162 (± 13)	641	221	31.1	2.5
26	0.60	2040	76	7.9	8.1	121 (± 7)	607	48	32.3	4.0
27	0.73	1880	74	4.6	8.3	105 (± 8)	550	0	48.8	2.7
28	0.62	2040	82	10.1	11.6	138 (± 9)	570	0	56.7	5.8

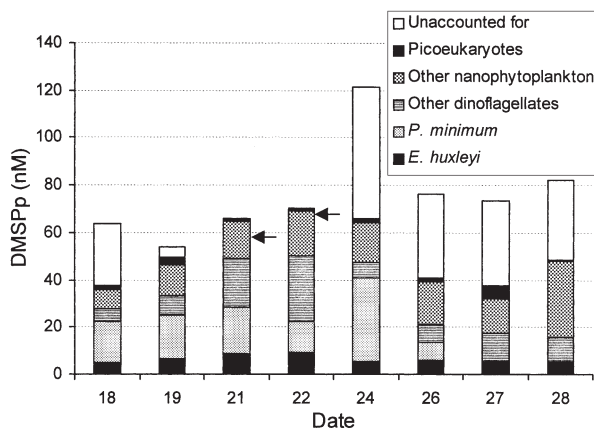


Fig. 1. Contribution of phytoplankton taxonomic groups to the DMSPP pool in waters used for the dilution experiments based on taxon-specific cell abundance and DMSPP cell content. DMSPP cell contents used in the analysis were: *Emiliana huxleyi*, 1.3 pg cell^{-1} (Keller et al. 1989, S.D.A. unpubl.); *Proocentrum minimum*, $21.4 \text{ pg cell}^{-1}$ (Keller et al. 1989); other dinoflagellates were allocated the same biomass-specific DMSPP content to *P. minimum* ($0.47 \text{ pg DMSPP pg}^{-1} \text{ C}$) and consist of cells enumerated and sized by microscopy that were larger than $10 \mu\text{m}$ in diameter; other nanophytoplankton were allocated a biomass-specific DMSPP content ($0.19 \text{ pg DMSPP pg}^{-1} \text{ C}$), half that of *E. huxleyi* and consisted of cells of 2 to $10 \mu\text{m}$ diameter enumerated by flow cytometry; eukaryotic picophytoplankton $0.0465 \text{ pg cell}^{-1}$ (Corn et al. 1996). The amount of measured DMSPP not accounted for by these phytoplankton groups is also shown. On 2 occasions the combined estimates of phytoplankton DMSPP exceed the measured values of total DMSPP as indicated by arrows

tions ranged from 17.8 to $33.2 \mu\text{g C l}^{-1} \text{ d}^{-1}$, equivalent to 1480 to 2770 nM C d^{-1} at the depths of water sampled for the dilution experiments (Table 1). These values are total rates of ^{14}C incorporation and as such include the synthesis of inorganic coccolithophore liths.

In the waters used for dilution experiments, microzooplankton biomass ranged from 25.5 to $56.7 \mu\text{g C l}^{-1}$ (Table 2). During the Lagrangian phase of the study, biomass was dominated by oligotrich ciliates; in particular a ciliate resembling *Strombidium ovale* (mean diameter $46 \mu\text{m}$) that occurred at an abundance of between 2500 and $8700 \text{ cells l}^{-1}$ (Table 2). Although similar concentrations of *S. ovale* occurred in the latter 3 experiments, heterotrophic dinoflagellates made up an increasingly higher proportion (38 to 59%) of the total microzooplankton biomass. Athecate heterotrophic dinoflagellates contributed the major proportion of biomass in samples from the Lagrangian phase and comprised both *Gymnodinium* spp. and *Gyrodinium* spp. The higher heterotrophic dinoflagellate biomass recorded on the other 3 dates was largely the result of increased thecate dinoflagellate abundance. In partic-

ular, on 27 and 28 June a large ($90 \mu\text{m}$ diameter) *Protopteridinium* sp. made up almost half of the heterotrophic dinoflagellate biomass.

DMSPP dynamics in dilution experiments

Apparent DMSPP production occurred in all incubations except on 24 June, when an apparent loss of DMSPP occurred in less dilute incubations (Fig. 2). In addition, increasing apparent growth of DMSPP occurred in response to increasing levels of dilution and therefore decreasing grazing pressure. The model I linear regression relationship between apparent growth of DMSPP and fraction of whole water was significant ($p < 0.05$) in all 8 experiments (Fig. 2, Table 3A).

Instantaneous growth rates of DMSPP in the absence of grazing (μ_{dmspp}) were calculated from the y-intercept of the regression. Estimates of μ_{dmspp} were similar between experiments, ranging from 0.26 to 0.58 d^{-1} (Table 3A). No DMSPP measurements were made in control incubations. However, based on the ratio of apparent chl *a* growth in undiluted waters to which nutrients were added (k_n) and control incubations to which no nutrients were added (k_c), estimates of the 'in situ' instantaneous growth rates of DMSPP ranged from 0.23 to 0.58 d^{-1} (Table 3A). This is equivalent to a total DMSPP doubling time of 1.2 to 3.0 d . 'In situ' DMSPP potential production increased over the first 4 d of the Lagrangian study from 14.8 to 45.6 nM d^{-1} and dropped to 25.5 nM d^{-1} on 24 June (Table 3A). On the 3 dates following the Lagrangian study DMSPP production averaged 25.0 nM d^{-1} (Table 3A).

The slope of the regression between apparent growth and fraction of whole water provides an estimate of the rate of DMSPP loss due to grazing (g_{dmspp}). Estimates of g_{dmspp} varied from 0.18 to 0.56 d^{-1} in the experiments (Table 3A). Values of g_{dmspp} suggest a turnover rate of DMSPP by microzooplankton grazers of 16 to $43\% \text{ d}^{-1}$ (turnover time of 6.2 to 2.3 d) during the Lagrangian study and an average of $29\% \text{ d}^{-1}$ (turnover time of 3.5 d) on the following 3 dates (Table 3A). This is equivalent to DMSPP losses of 11.4 to 59.9 nM d^{-1} during the Lagrangian study and an average of 27.9 nM d^{-1} at the other 3 stations. Potential production rates of DMSPP based on the 'in situ' values generally exceeded rates of loss due to grazing during the Lagrangian study (Table 3A). The amount of DMSPP consumed by microzooplankton averaged $62\% \text{ d}^{-1}$ of potential production during the first 4 d of the Lagrangian phase but increased dramatically on 24 June to almost $200\% \text{ d}^{-1}$. On the 27 and 28 June, all potential DMSPP production was consumed by grazers (Table 3A).

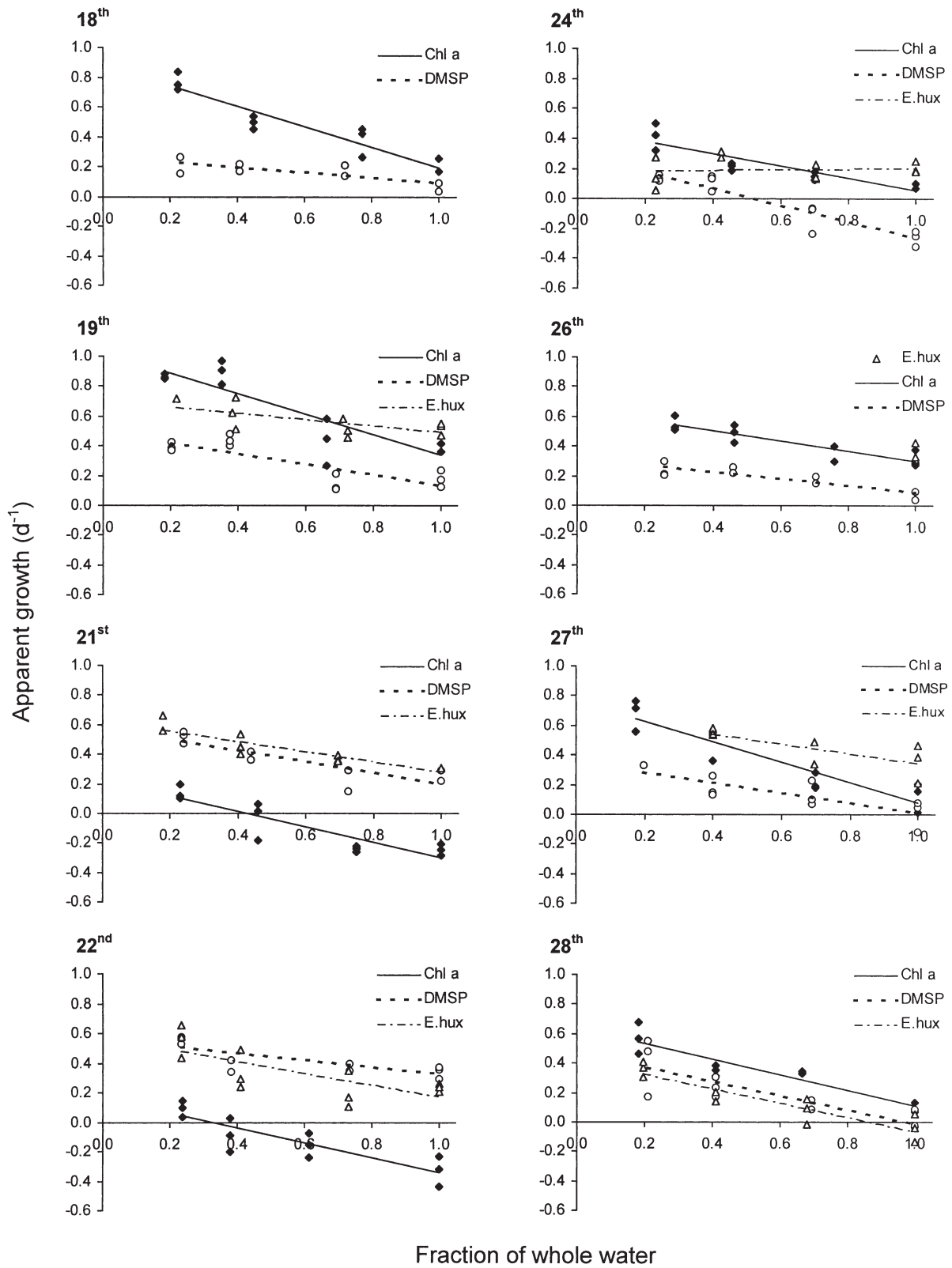


Fig. 2. Relationship between apparent change in DMSP_p, chl a and *Emiliana huxleyi* and the level of dilution (fraction of whole water) in the 8 dilution experiments in June. The values of the regression analyses are given in Table 3

Table 3. Instantaneous growth rate (μ) and loss due to grazing (g) calculated from the regression between apparent growth and dilution factor (Fig. 2) for (A) DMSPp (nM), (B) chl *a* ($\mu\text{g l}^{-1}$) and (C) *Emiliana huxleyi* ($\times 10^3$ cells l^{-1}). Values of μ_n and μ_c are rates in incubations with nutrient addition and corrected to 'in situ' rates based on control incubations with no nutrient addition, respectively. p is the significance of the F -ratio of the analysis of variance of the model 1 regression of each dilution experiment. The mean concentration ($\hat{c} = [C_t - C_0]/[\ln C_t - \ln C_0]$), potential production ($P_p = \mu_c \cdot \hat{c}$), production consumed ($P_c = g \cdot \hat{c}$) and % of production grazed [$P_g = (\mu_c/g) \cdot 100$] and turnover rates ($= 1 - e^{-g} \cdot 100$) are shown. μ_n dmosp were adjusted to μ_c dmosp according to the ratio $\mu_c:\mu_n$ calculated from chl *a* analyses (see [B]). *No significant difference (t -test, $p < 0.05$) between triplicate controls and nutrient addition incubations; **no control incubations analysed; ***net growth rate in undiluted water. ns: not significant; nd: no data

Day in June	μ_n (d^{-1})	μ_c (d^{-1})	g (d^{-1})	p	\hat{c}	P_p (d^{-1})	P_c (d^{-1})	P_g (% d^{-1})	Turnover (% d^{-1})
(A) DMSPp									
18	0.26 (± 0.04)	0.23	0.18 (± 0.06)	0.023	65	14.8	11.4	67	16
19	0.49 (± 0.05)	0.41	0.35 (± 0.08)	0.001	59	24.5	20.9	72	30
21	0.58 (± 0.06)	0.58*	0.38 (± 0.09)	0.003	67	38.9	25.6	66	32
22	0.56 (± 0.04)	0.56*	0.24 (± 0.07)	0.007	81	45.6	19.1	42	21
24	0.29 (± 0.04)	0.24	0.56 (± 0.06)	0.000	107	25.5	59.9	192	43
26	0.32 (± 0.03)	0.32*	0.23 (± 0.05)	0.001	79	25.0	18.4	74	21
27	0.35 (± 0.07)	0.25	0.34 (± 0.09)	0.007	74	18.3	25.2	98	29
28	0.47 (± 0.07)	0.38	0.48 (± 0.10)	0.001	83	31.6	40.1	103	38
(B) Chlorophyll a									
18	0.87 (± 0.06)	0.75	0.67 (± 0.09)	0.000	0.44	0.332	0.299	90	49
19	1.03 (± 0.08)	0.87	0.69 (± 0.14)	0.000	0.49	0.428	0.335	78	49
21	0.23 (± 0.06)	0.23*	0.53 (± 0.10)	0.000	0.81	0.180	0.424	235	41
22	0.19 (± 0.06)	0.19*	0.57 (± 0.10)	0.000	0.88	0.142	0.441	311	40
24	0.46 (± 0.05)	0.34	0.40 (± 0.07)	0.000	0.73	0.378	0.289	77	33
26	0.66 (± 0.04)	0.66*	0.38 (± 0.05)	0.000	0.70	0.451	0.239	53	29
27	0.79 (± 0.06)	0.56	0.75 (± 0.09)	0.000	0.69	0.385	0.475	123	50
28	0.64 (± 0.05)	0.52	0.54 (± 0.08)	0.000	0.62	0.322	0.326	101	41
(C) <i>Emiliana huxleyi</i>									
18	nd	nd	nd	nd	nd	nd	nd	nd	nd
19	0.72 (± 0.06)	0.72**	0.24 (± 0.01)	0.039	872	629	212	34	22
21	0.64 (± 0.04)	0.54	0.37 (± 0.07)	0.001	998	537	373	69	31
22	0.58 (± 0.09)	0.58*	0.42 (± 0.14)	0.015	1099	637	459	72	34
24	0.19 (± 0.06)	0.19*	ns	0.810	nd	nd	nd	nd	nd
26	0.36 (± 0.06)	0.36***	nd	0.044	735	nd	nd	nd	nd
27	0.69 (± 0.10)	0.69*	0.36 (± 0.14)	0.054	667	459	241	53	30
28	0.43 (± 0.05)	0.12	0.50 (± 0.09)	0.000	479	59	238	401	39

Chl *a* dynamics in dilution experiments

The model I linear regression relationship between apparent growth of chl *a* and fraction of whole water was highly significant ($p < 0.001$) in all 8 experiments (Fig. 2, Table 3B). Significant differences (t -test, $p < 0.05$) between apparent growth rate in undiluted incubations with (k_n) and without (k_c) added nutrients occurred in 5 of the 8 experiments. The ratio between measured (μ_n) and adjusted instantaneous growth rate (μ_c) varied from 0.71 to 1.00 in the 5 experiments. Adjusted 'in situ' μ_{chl} ranged from 0.19 to 0.87 d^{-1} during the Lagrangian study and from 0.52 to 0.66 d^{-1} on the following 3 d. These values represent a potential production of 0.14 to 0.43 $\mu\text{g chl a l}^{-1} \text{d}^{-1}$ during the Lagrangian period and 0.32 to 0.45 $\mu\text{g chl a l}^{-1} \text{d}^{-1}$ on subsequent dates (Table 3B). Values of the coefficient of mortality rate due to microzooplankton grazing (g_{chl})

decreased during the Lagrangian period, with resulting turnover rates of 49 to 33% d^{-1} (turnover times of 2.0 to 3.0 d) (Table 3B). However, the quantity of production that was consumed remained similar, ranging from 0.29 to 0.44 $\mu\text{g chl a l}^{-1} \text{d}^{-1}$ on the dates of the Lagrangian study and 0.24 to 0.48 $\mu\text{g chl a l}^{-1} \text{d}^{-1}$ on the following days (Table 3B). Low rates of potential production on 21 and 22 June largely explain the imbalance between the potential production and production consumed on those dates. On the remaining dates potential production matched or exceeded the rates of consumption by microzooplankton (Table 3B).

Emiliana huxleyi dynamics in dilution experiments

The model I regression between apparent growth of *Emiliana huxleyi* and fraction of whole water was sig-

nificant ($p < 0.05$) on 5 of the 6 days on which cell counts were conducted. Apparent growth of *E. huxleyi* in undiluted incubations did not react to nutrient addition in the same way as chl *a*. In only 2 of the 5 experiments in which k_c for *E. huxleyi* was determined did significant differences occur between k_c and k_n . Values of k_c were not determined on 19 June, and therefore μ_{Ehux} may be overestimated on that date. In addition, incomplete counts of the most dilute incubations on 27 June resulted in estimates of net growth for only 3 levels of dilution. On the 3 dates during the Lagrangian study on which significant regression results were obtained, instantaneous growth rates were close to 1 doubling d^{-1} and represented similar potential production rates of 537 to 637×10^3 cells $\text{l}^{-1} \text{d}^{-1}$ (Table 3C). A similar rate of growth and potential production occurred on 27 June. On 28 June, a ratio for $\mu_c:\mu_n$ of 0.24 reduced the instantaneous rate of growth to 0.12 d^{-1} , equivalent to a potential production of only 59×10^3 cells $\text{l}^{-1} \text{d}^{-1}$ (Table 3C). In general, rates of mortality due to microzooplankton grazing were lower than potential production and represented a similar rate of turnover of 22 to 39% d^{-1} of the initial standing stock (turnover time of 2.6 to 4.6 d) in all 5 experiments (Table 3C).

Comparison of growth rates

Apparent rates of DMSPp growth were not measured in control incubations, and values of μ_{dmSP} were adjusted to 'in situ' rates based on the differences in net production of chl *a* in control and nutrient amended incubations. However, it is possible that the DMSPp producing phytoplankton reacted differently to nutrient addition than the bulk community represented by chl *a*. Instantaneous growth rates not adjusted for potential nutrient limitation averaged $0.41 (\pm 0.12) \text{ d}^{-1}$ for DMSPp, $0.54 (\pm 0.18) \text{ d}^{-1}$ for *Emiliania huxleyi* and $0.60 (\pm 0.30) \text{ d}^{-1}$ for chl *a*. The mean rates once values were adjusted to 'in situ' nutrient levels were $0.37 (\pm 0.14)$, $0.47 (\pm 0.26)$ and $0.53 (\pm 0.24) \text{ d}^{-1}$, respectively. The adjusted values represent a mean doubling time of 1.9, 1.5 and 1.3 d, respectively. When either nutrient addition or 'in situ' values of μ are compared (Fig. 3A), μ_{dmSP} was lower than μ_{chl} , except on 21 and 22 June, when μ_{dmSP} exceeded the rates for chl *a* largely due to lower growth rates of chl *a* (Table 3). When 'in situ' values of μ are compared, μ_{Ehux} was also higher than μ_{chl} on the 21 and 22 June, but similar to or lower on 19, 27, 28 June (Table 3, Fig. 3A). If 'in situ' values are compared, μ_{dmSP} was lower than or similar to μ_{Ehux} except on 28 June, when low rates of net growth of *E. huxleyi* in control incubations reduced μ_{Ehux} from 0.47 to 0.12 d^{-1} (Fig. 3A).

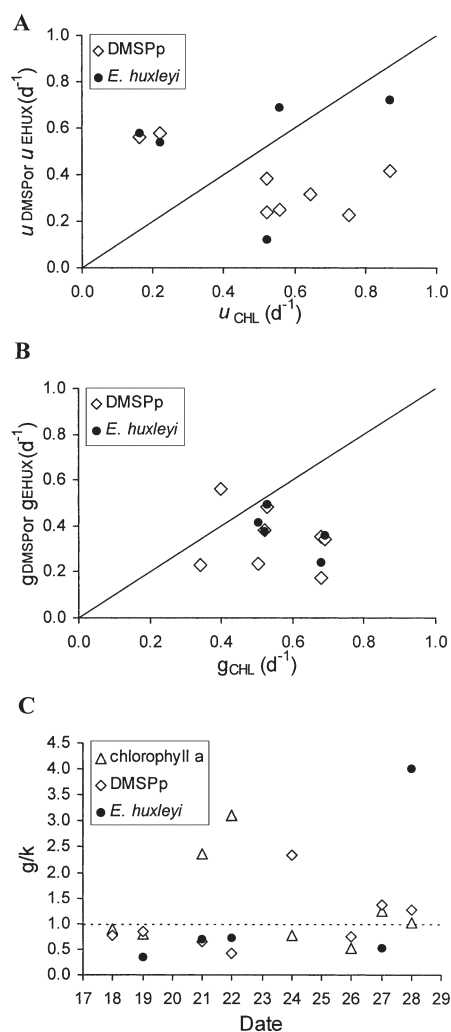


Fig. 3. Growth (A) and grazing (B) coefficients of DMSPp and *Emiliania huxleyi* compared to chl *a* and (C) the proportion of production grazed (g/k) for chl *a*, DMSPp and *E. huxleyi* on each experimental date. The lines in (A) and (B) represent identical growth and grazing rates to chl *a*, and in (C) the dotted line represents growth rates balanced by grazing rates

Comparison of mortality rates due to grazing

The slope of the regression (g) for the level of dilution versus DMSPp and *Emiliania huxleyi* was generally lower than that of chl *a* (Fig. 3B). In 4 of the 8 experiments, g_{dmSP} was significantly lower ($p < 0.05$) than g_{chl} and was not significantly different from g_{Ehux} on 4 of 5 comparisons (Table 4). Mean values of g during the study were $0.35 (\pm 0.13) \text{ d}^{-1}$ for DMSPp, $0.36 (\pm 0.10) \text{ d}^{-1}$ for *E. huxleyi* and $0.54 (\pm 0.13) \text{ d}^{-1}$ for chl *a*. This is equivalent to mean turnover rates of $30.6 (\pm 9.0)$, $29.7 (\pm 6.9)$ and $40.3 (\pm 7.8) \% \text{ d}^{-1}$, respectively.

Table 4. Comparison of coefficients of mortality (g) for chlorophyll a (chl a), DMSPp and *Emiliania huxleyi*. Values are the level of significance of an F -test for the difference between pairs of regression coefficients (Sokal & Rohlf 1995): similar = no significant difference at $p < 0.05$; nd = no data

Day in June		DMSPp	<i>E. huxleyi</i>
18	Chl a	$p < 0.001$	nd
	<i>E. huxleyi</i>	nd	
19	Chl a	$p < 0.05$	$p < 0.025$
	<i>E. huxleyi</i>	Similar	
21	Chl a	Similar	Similar
	<i>E. huxleyi</i>	Similar	
22	Chl a	$p < 0.01$	Similar
	<i>E. huxleyi</i>	Similar	
24	Chl a	Similar	$p < 0.001$
	<i>E. huxleyi</i>	$p < 0.001$	
26	Chl a	Similar	nd
	<i>E. huxleyi</i>	nd	
27	Chl a	$p < 0.01$	$p < 0.025$
	<i>E. huxleyi</i>	nd	
28	Chl a	Similar	Similar
	<i>E. huxleyi</i>	Similar	

DISCUSSION

In surface waters of the northern North Sea containing DMSP-rich phytoplankton, DMSPp production rates estimated by the dilution approach ranged from 14.8 to 45.6 nM d⁻¹ and represent a doubling time of the ambient DMSPp pool of between 1.2 and 3.1 d (Table 3A). Consumption rates of DMSPp by microzooplankton varied between 11.4 and 59.9 nM d⁻¹ and were equivalent to turnover rates of the ambient DMSPp pool of between 16 and 43% d⁻¹ (Table 3A). The high significance of the regression analyses (generally $p < 0.01$; Fig. 2, Table 3A) on which these production and consumption values are based indicates that they are robust and meaningful.

One way to gauge how tenable the values are is to compare them to 3 other studies that have measured DMSPp production/consumption rates (Table 5). Wolfe et al. (2000) measured net changes in DMSPp using a similar dilution approach to the present study. In 2 experiments conducted on the Newfoundland and Labrador shelf, the regression analyses of the dilution plots appear to be significant ($p \leq 0.05$, $n = 8$, $r^2 = 0.50$) and instantaneous growth rates of the phytoplankton community based on chl a were positive. Values of μ_{dmSP} were 0.47 and 0.18 d⁻¹ and for g_{dmSP} were 0.10 and 0.22 d⁻¹ from these 2 experiments. Using these data, production and consumption rates of DMSPp can be calculated (Table 5) that are equivalent to DMSPp doubling times of 1.5 and 3.9 d and a turnover rate of 10 and 20% d⁻¹, respectively. Water temperatures were lower (-0.1 and -0.4°C) and chl a concentrations higher (5.6 and 1.4 $\mu\text{g l}^{-1}$) than in the present study, and differences in the phytoplankton community structure may account for the microzooplankton consumption rates being lower than those found in the present study. Nevertheless, the results are comparable to those measured in the northern North Sea in summer.

During early spring off the Washington Coast, estimates of DMSPp production based on the incorporation rate of ³⁵SO₄²⁻ (Table 5) are likely to have been underestimates due to probable losses during sample filtration and freezing (Bates et al. 1994). Despite this, the deeply mixed (60 m) water column and a phytoplankton community dominated by picoplankton, particularly *Synechococcus* spp., the DMSPp production rates still represent 10% d⁻¹ of the DMSPp standing stock. DMSPp production rates in the present study averaged 40% d⁻¹ of the standing stock.

Similar rates of DMSPp production to the present study were obtained by budgeting concentrations and transformation rates of total DMSP (dissolved + particulate) between Lagrangian samplings (Table 5) (Simó & Pedrós-Alió 1999). These estimates were carried out

Table 5. Comparable estimates of rates of DMSPp production and turnover

Method	Location	Depth (m)	Chl a ($\mu\text{g l}^{-1}$)	DMSP (nM)	DMSPp production (nM d ⁻¹)	DMSPp turnover (nM d ⁻¹)	Source
Dilution approach	Newfoundland and Labrador shelf	3	5.6	46	26	6	Wolfe et al. (2000)
		20	1.4	112	21	26	
³⁵ SO ₄ ²⁻ uptake	NE Pacific waters	Average for top 60 m	<0.4	16.7	1.8	3.8 (based on carbon turnover)	Bates et al. (1994)
Incubations plus Lagrangian expt	Iceland Basin	Surface	0.85–0.50	30–50	11.3–30.9	8.1–50.6 (total DMSP)	Simó & Pedrós-Alió (1999)
Dilution approach	Northern North Sea	5–10	0.40–1.03	54–121	14.8–45.6	11.4–59.9	Present study

during an SF₆ Lagrangian experiment in an anticyclonic eddy in the Iceland Basin with surface waters containing numbers of *Emiliania huxleyi*, levels of DMSPp and chl *a* concentrations similar to the present study. The consumption rates of total DMSP were calculated from the decrease in total DMSP concentration during dark incubations (Simó & Pedrós-Alió 1999). These values encompass all processes that involve a DMSP loss, including grazer assimilation, algal and bacterial cleavage, bacterial demethylation and bacterial assimilation. The similar rates of DMSPp consumption between the 2 studies (Table 5) suggests that in waters characterised by low chl *a* concentrations and abundant *E. huxleyi*, microzooplankton may be the principal agents of DMSPp transformation. They are likely to assimilate a proportion of the DMSP themselves, provide a supply of dissolved DMSPd which bacteria may metabolise and also possibly produce DMS as a result of the DMSP lyase enzymes of ingested algal cells.

What do μ_{dmSP} and g_{dmSP} represent?

Although the results of DMSPp production and turnover rates determined by the dilution approach are tenable, it is important to explore what they represent and potential errors in the approach. The determination of DMSP production and turnover by the dilution approach assumes that DMSPp measured on GF/F filters exclusively comprises DMSP within phytoplankton cells. However, bacteria (Diaz et al. 1992), heterotrophic protozoans (Ishida 1996), copepods (Kwint et al. 1996, Tang et al. 1999) and detrital material including copepod faecal pellets (Kwint et al. 1996) may contain DMSP. In an attempt to identify the phytoplankton group-specific sources of DMSPp (Fig. 1), the predicted DMSPp contribution of the phytoplankton accounts for the total DMSPp measured on 3 dates during the Lagrangian period. In contrast, on the remaining dates up to 49% of the measured DMSPp could not be accounted for (Fig. 1). This suggests that other components of the <200 μm plankton may make up a substantial proportion of the DMSPp. However, it is likely that the taxon-specific DMSP cell content used in the estimates differs from those encountered in natural waters, and this may, in part, account for the shortfall in partitioning total DMSPp. In addition, unidentified components of the phytoplankton may be important contributors to the DMSPp pool, and delicate phytoplankton cells may be lost due to preservation. However, if a large proportion of DMSPp is contained in other particles, then measurements of apparent net change in DMSPp in the dilution experiments may not represent net production of only phytoplankton DMSP,

with implications for estimates of instantaneous DMSPp production and turnover.

Few estimates of bacterial DMSPp have been made in natural waters, and it was not measured in the present study. However, the bacterial carbon biomass in surface waters during the Lagrangian experiment averaged 374 nM, and bacteria have been found to rapidly consume DMSPd (Zubkov et al. 2001). If bacteria were able to sequester DMSP to the same levels as DMSP-rich phytoplankton (about 10% of total cell carbon), an upper limit of the bacterial DMSPp contribution would be close to 7 nM or about 10% of the total DMSPp. These estimates are supported by measurements of DMSP in water collected from the Mediterranean and the tropical North Atlantic, where the contribution of bacteria-sized particles (0.2 to 1.0 and 0.2 to 2.0 μm , respectively) was approximately 10% of total DMSPp (Belviso et al. 1993). In dilution experiments, bacterioplankton generally grow faster than co-occurring phytoplankton and are grazed at a correspondingly higher rate (Archer et al. 2001). As a result, de novo synthesis and turnover of phytoplankton DMSPp may be overestimated.

Whether natural populations of microzooplankton, including dinoflagellate taxa, incorporate or synthesise DMSP remains to be discovered. The dinoflagellate *Cryptecodinium cohnii*, when grown heterotrophically in culture, is able to synthesise DMSP (Uchida et al. 1996). It is possible that microzooplankton represent a sizeable pool of DMSPp. The presence of undegraded pigment sequestered within microzooplankton at the beginning of dilution incubations may cause an underestimate of phytoplankton growth rates based on pigment analyses (Waterhouse & Welschmeyer 1995). Similarly, DMSP contained in microzooplankton at the start of experiments may lead to an underestimate of apparent phytoplankton DMSP production. Furthermore, the dilution approach relies on the assumption that phytoplankton mortality due to grazing is proportional to the dilution effect on grazer abundance (Landry & Hassett 1982), and therefore it follows that levels of microzooplankton DMSP would be expected to alter in proportion to the level of dilution. However, if microzooplankton abundance alters disproportionately to the level of dilution (e.g. Dolan et al. 2000), it may have implications on both the estimates of mortality due to grazing and the net DMSPp production rates.

In summary, the largest uncertainty in the estimates of phytoplankton DMSPp production and turnover most likely stems from the influence of other particles that contain DMSP. Bacterial sequestration of DMSP may lead to an overestimation of the apparent DMSPp growth rates and therefore overestimates of μ_{dmSP} and possibly g_{dmSP} . Alternatively, if DMSP is contained in microzooplankton or detrital matter at the start of incu-

bations, apparent phytoplankton DMSP growth rates may be underestimated. Further studies, possibly involving laboratory culture experiments, are required to fully understand the influence of other forms of DMSPp on estimates of net phytoplankton DMSP growth and, hence, to define μ_{dmSP} and g_{dmSP} . In the remainder of the discussion, μ_{dmSP} and g_{dmSP} are assumed to represent instantaneous growth and mortality of phytoplankton DMSP.

DMSPp producers and the phytoplankton community

The rates of DMSPp production calculated from the dilution experiments were found to be closely correlated to estimates of ^{14}C primary production (Fig. 4). Both ^{14}C incorporation rates and the estimates of DMSPp production based on values of μ_{dmSP} are likely to underestimate gross production. However, the close coupling between them lends support to the significance of the values of μ_{dmSP} and therefore g_{dmSP} and to the view that DMSPp production is chiefly a product of phytoplankton synthesis. Based on the linear regression between ^{14}C production and DMSPp production (Fig. 4), DMSPp production rates in the 8 dilution experiments are equivalent to $10.8 (\pm 2.4 \text{ SE}) \%$ of the carbon fixed by phytoplankton. This is consistent with estimates of the contribution of DMSP to cellular carbon of $>10\%$ in species that produce significant amounts of DMSP (Matrai & Keller 1994) and reasonable for a phytoplankton community dominated by DMSP-rich phytoplankton. Using the same regression values (Fig. 4), the molar ratio of production of carbon:sulphur was $45.5 (\pm 10.3 \text{ SE})$, where the sulphur production accounted for is purely in the form of DMSP. This is in good agreement with estimates of the C:S molar ratio of DMSP-rich phytoplankton in culture. The organic C:S molar ratios of cells of 3 DMSP-rich

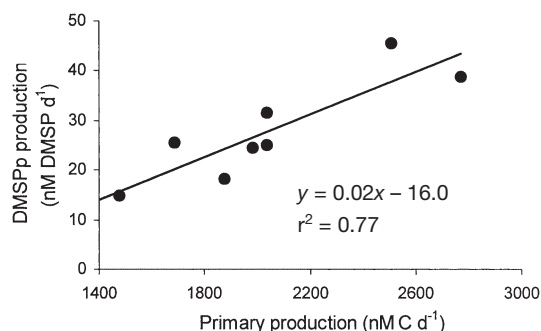


Fig. 4. Relationship between the potential production of DMSPp (Pp, Table 3A) with primary production measured as ^{14}C incorporation (Table 1). Dilution experiments and primary production incubations were carried out using water collected at the same depth and times

phytoplankton—*Amphidinium carterae*, *Prorocentrum minimum* and *Emiliana huxleyi*—in culture were 56, 48 and 80, respectively (Matrai & Keller 1994). DMSP accounted for the majority (50 to 100%) of the particulate organic sulphur in these taxa.

It may be possible to judge how the dynamics of DMSP producing phytoplankton differ from those of the bulk phytoplankton community by comparing estimates of growth and mortality for chl *a*, *Emiliana huxleyi* and DMSPp. In general, the rates of turnover of DMSPp and *E. huxleyi* were similar and lower than for chl *a* (Table 4, Fig. 3B). This indicates that grazing pressure on DMSPp-containing phytoplankton, including *E. huxleyi*, was lower than that on the bulk phytoplankton community and may lend support to the suggestion by Wolfe et al. (1997) that DMSP acts as part of a grazing-deterrence mechanism. However, in dilution experiments in which the net production of a variety of phytoplankton pigments is determined, varying degradation rates for different compounds are thought to complicate comparisons of taxon-specific mortality (Waterhouse & Welshmeyer 1995). If DMSP is sequestered or incompletely degraded by microzooplankton, then turnover rates may be underestimated. Similarly, it could be argued that the higher turnover rates determined for chl *a* than for DMSPp (Table 4, Fig. 3B) may be the result of more complete chl *a* degradation during digestion and lower levels of chl *a* incorporation into microzooplankton cells rather than selectivity against DMSP producing algae. Direct cell counts may be the most accurate measure of net growth and therefore grazing mortality in dilution experiments, although they do not account for changes in cell volume/biomass that may occur as part of the phytoplankton growth (Verity et al. 1996). In the 5 experiments in which the mortality due to grazing on *E. huxleyi* (g_{Ehux}) was determined, it differed significantly from g_{dmSP} on only 1 occasion and was significantly lower than g_{chl} on 3 dates (Table 4, Fig. 3B). The similar rates of grazing mortality of *E. huxleyi* cells and DMSPp are somewhat surprising considering the relatively low proportion of DMSPp contributed by *E. huxleyi*, the variety of phytoplankton taxa that contributed to the DMSPp pool (see above) and probable variations in DMSP-lyase activity between phytoplankton taxa. They suggest that the grazing pressure on the bulk of the DMSPp-containing phytoplankton population was similar to that on *E. huxleyi*. Protozoan grazers select prey partly on the basis of size (e.g. Fenchel 1980). The size range of abundant DMSP-containing phytoplankton was known to vary 3 fold, from *Prorocentrum minimum* (15 μm diameter), which contributed an estimated 0 to 35% of the DMSPp, to *E. huxleyi* (~5 μm diameter), and may have been grazed by different taxa of microzooplankton. However, the dominant compo-

ment of the microzooplankton communities present in the experiments was an oligotrich ciliate resembling *Strombidium ovale*, ~50 µm in length, which alone accounted for 11 to 51 % of the total microzooplankton biomass. It seems likely that the *S. ovale*-type ciliates were capable of ingesting almost the complete size range of DMSP-containing phytoplankton, including *E. huxleyi*, *P. minimum* and the other nanophytoplankton that also probably contributed to the DMSPp pool; this may account for the similar turnover rates of DMSPp and *E. huxleyi*.

It is possible to estimate the contribution of *Emiliana huxleyi* to the production and consumption of DMSPp based on a constant DMSP content of 1.3 pg cell⁻¹ (see above and Fig. 1). The potential production of DMSPp by *E. huxleyi* (Table 3C) varied between 25 % of the total DMSPp production on 19 June and 2 % on 28 June. Similarly, the rate of consumption of *E. huxleyi* represented 6 to 23 % of the total DMSPp consumed. Obviously, other phytoplankton contributed substantially to the DMSPp production and turnover.

Microzooplankton assimilation and transformation of DMSPp

There is growing evidence that DMSP is of nutritional importance to planktonic heterotrophic organisms. Dissolved DMSP is potentially an important sulphur and carbon source for bacterioplankton (Kiene & Linn 2000, Zubkov et al. 2001), and dietary DMSP may be incorporated into the tissues of a variety of copepods (Tang et al. 1999). In addition, a large amount of research has focussed on the tissue content of DMSP in seafood (e.g. Iida & Tokunaga 1986) and use of DMSP as a feeding and/or growth stimulant in cultured fish and shellfish (e.g. Nakajima 1991). DMSP may be an

equally important component of microzooplankton diets. If DMSP or DMS are of nutritional value, they may be assimilated by the microzooplankton with a degree of assimilation in part dependent on their carbon and sulphur demands and directly affecting the level of production of DMSPd and/or DMS. The dilution approach has been used to directly quantify the rates of release of DMS and DMSPd from microzooplankton grazers in natural waters (Archer et al. 2001). This approach is not always practicable due to changes in the dissolved pool of DMSPd and DMS that may result from the filtration procedures required for the experiments (Archer et al. 2001). As a more straightforward alternative, it may be possible to estimate the production of dissolved DMS+DMSPd from the levels of ingestion of DMSPp measured in the present study.

Assuming a microzooplankton gross production rate of 0.4 d⁻¹, a gross growth efficiency of 0.3 (Straile 1997), and carbon:sulphur molar ratio of 80, equivalent to DMSP-rich phytoplankton (Matrai & Keller 1994), it is possible to approximate the microzooplankton carbon and sulphur demands (Table 6). Except on 24 June, when DMSP ingestion rates were exceptionally high relative to microzooplankton biomass (Table 3A), DMSPp possibly contributed 2 to 3 % of the microzooplankton carbon requirements and 26 to 44 % of their sulphur demand (Table 6). A key value in these calculations is the DMSPp assimilation efficiency, as it has a direct bearing on the quantity of DMSP and DMS released into solution. A gross growth efficiency of 0.3 implies the release of 70 % of ingested DMSPp either as DMSP in faecal pellets, DMSPd, DMS and acrylate or alternative by-products of digestion. Several laboratory studies suggest this level of release may be a fair approximation. More than 66 % of ingested DMSP contained in the prymnesiophyte *Isochrysis galbana* was released to solution when consumed by the ciliate

Table 6. The potential contribution of DMSPp to carbon and sulphur demands of microzooplankton (MZP) and the quantity of DMSPp potentially released to solution as DMSPd or DMS. The ingested carbon and sulphur demands of MZP are based on a specific growth rate of 0.4 d⁻¹ and a gross growth efficiency of 0.3. An MZP carbon:sulphur molar ratio of 80 was assumed to calculate sulphur demand (see text for further details)

Day in June	Ingested carbon demand (µg C l ⁻¹ d ⁻¹)	Ingested sulphur demand (µg S l ⁻¹ d ⁻¹)	DMSPp contribution to carbon demand (%)	DMSPp contribution to sulphur demand (%)	'DMSP' released (nM d ⁻¹)	MZP biomass-specific 'DMSP' release (nM µg C ⁻¹ d ⁻¹)
18	42	1.4	2	26	8.0	0.31
19	46	1.5	3	44	14.7	0.52
21	67	2.2	2	37	17.9	0.44
22	62	2.1	2	30	13.4	0.36
24	51	1.7	7	113	41.9	1.35
26	53	1.8	2	33	12.8	0.40
27	80	2.7	2	30	17.6	0.36
28	93	3.1	3	41	28.1	0.49

Strombidium sulcatum (Christaki et al. 1996). Wolfe et al. (1997) found that the DMSP-lyase activity of ingested *E. huxleyi* affected the level of production of DMS when ingested by the dinoflagellate *Oxyrrhis marina*. When strains with high lyase activity were consumed, approximately 60% of ingested DMSPp was converted to DMS. If in the present study 70% of ingested DMSPp was released to solution, then DMSPd+DMS production due to microzooplankton grazing would amount to 8.0 to 41.9 nM d⁻¹ (Table 6). This is equivalent to a microzooplankton biomass specific production of 0.31 to 0.52 nM S µg C⁻¹ d⁻¹ in 7 of the experiments and 1.35 nM S µg C⁻¹ d⁻¹ on 24 June (Table 6). Comparable values of 0.39 to 0.65 nM S µg C⁻¹ d⁻¹ were determined by using the dilution approach to directly estimate DMS+DMSPd production rates in waters of the Iceland Basin (Archer et al. 2001). Phytoplankton and microzooplankton communities were similar to the present study, with concentrations of DMSPp, chl *a* and microzooplankton biomass of 93 to 125 nM, 1.4 µg l⁻¹ and 21.9 to 25.3 µg C l⁻¹, respectively. This suggests that in DMSP-rich, nanophytoplankton-dominated waters, the role of microzooplankton in transforming DMSPp to solution may be predicted on the basis of microzooplankton biomass.

Conclusions

The standing stocks of DMSPp in the undiluted waters used for dilution experiments averaged 77 nM, with DMSPp production levels of 39% d⁻¹ of the standing stocks closely matched by microzooplankton ingestion rates (Fig. 5). The ambient concentrations of

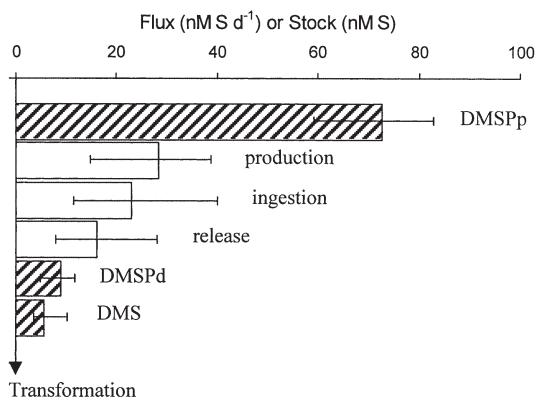


Fig. 5. Average values of the stocks of DMSPp, DMSPd and DMS and the rates of DMSPp production, ingestion by microzooplankton and potential release to solution determined in 7 dilution experiments. The bars show the range of values measured. Values are not included from the experiment on 24 June when both DMSPp concentration and DMSPp consumption were more than 3 × SD greater than the mean values

DMSPd and DMS in the water at the start of dilution experiments were 4.9 to 11.6 and 3.7 to 10.1 nM, respectively (Table 2). The level of release of the equivalent of 8.0 to 41.9 nM d⁻¹ of DMSPp following digestion (Table 6) suggests that microzooplankton grazing transforms sufficient DMSPp to solution to support a daily turnover of the DMSPd and DMS stocks (Fig. 5). In order to improve predictive models of DMS production, it would be useful to address the degree of assimilation of DMSP and DMS by microzooplankton and the factors that influence this in natural waters. These results illustrate the value of the dilution approach for examining the initial stages in the complex network of processes that lead to DMS production. For a more complete understanding of these processes, the approach needs to be applied to the various planktonic environments considered to be important producers of DMS. The approach may also be applicable to elucidating the production and fate of other key phytoplankton metabolites.

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