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Phytoplankton taxa, irradiance and nutrient availability determine the seasonal cycle of DMSP in temperate shelf seas

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ABSTRACT: The influences of physico-chemical and biological variables on the concentrations of dimethyl sulphide (DMS) and its precursor β-dimethylsulphoniopropionate (DMSP) were investigated through an annual cycle in the temperate shelf seas of the western English Channel. Total DMSP to chlorophyll *a* ratios (DMSPt/chl *a*) varied seasonally by 40-fold, and DMS and DMSP concentrations became temporally uncoupled, with elevated relative DMS concentrations during spring and mid-summer. Taxonomic succession of high DMSP-producing phytoplankton, including *Phaeocystis pouchetii*, *Scrippsiella trochoidea* and *Prorocentrum minimum*, is apparent in the seasonal pattern of DMSPt concentrations. Peridinin and DMSPt concentrations showed similar seasonal trends ($p < 0.0001$), illustrating the substantial contribution by dinoflagellate taxa to DMSP production. Summertime stratification of the water column coincided with increased mixed layer doses of photosynthetically active radiation (PAR), increased surface ultraviolet-B (UVB) irradiance relative to PAR and a decrease in nitrate and phosphate availability. PAR dose explained 68% of the variability in DMSP/chl *a* during the seasonal study; whilst nitrate concentrations were inversely related to DMSP/chl *a* and explained 64% of the variability in log-transformed DMSP/chl *a*. PAR dose explained only 25% of the variation in DMS concentration, whilst nitrate concentration was inversely related to DMS and explained 49% of the variation in log-transformed DMS concentration. The highly significant relationship between DMSP/chl *a* and PAR dose was similar to those observed for the chlorophyll-specific accumulation of the photoprotective xanthophyll compounds diadinoxanthin and diatoxanthin and the chlorophyll-specific concentrations of UV-absorbing mycosporine-like amino acids. These results lend further, indirect evidence for a photoprotective role of DMSP, possibly associated with physiological stress caused by high PAR and UV radiation and intensified by nutrient limitation.

KEY WORDS: DMSP · DMS · Seasonal cycle · Xanthophyll pigments · MAAs · Nutrients

INTRODUCTION

Emission of dimethyl sulphide (DMS) from the oceans may contribute to the nucleation and growth of aerosol particles, enhancing formation of cloud condensation nuclei (CCN) in the marine boundary layer and, thereby, increasing the Earth's albedo (Shaw 1983, Charlson et al. 1987). Once in the atmosphere, the oxidation pathway of DMS is likely to influence the link between DMS and CCN formation. This includes possible reactions with the photolysis products of biogenic halocarbons, and the presence of pre-existing sea-salt and organic aerosol particles (O'Dowd et al. 2002, von Glasow & Crutzen 2004, Leck & Bigg 2005). DMS is generally supersaturated in oceanic waters, and its sea to air flux is dictated to a large extent by seawater surface concentration and the gas transfer velocity. DMS is a product of the enzymatic cleavage of the S-containing osmolyte β-dimethylsulphoniopropionate (DMSP), synthesised by a variety of phytoplankton (Challenger & Simpson 1948, Keller et al. 1989). Intracellular concentrations of DMSP in phytoplankton

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vary by >3 orders of magnitude (Keller et al. 1989), and the ability to convert DMSP into DMS through DMSP-lyase activity also varies markedly between phytoplankton taxa (Niki et al. 2000). DMSP appears to play a range of roles in phytoplankton, in addition to acting as an osmolyte or compatible solute (Stefels 2000). Which physiological function(s) drive(s) the taxonomic variation in DMSP intracellular content remains unclear and is one of the hurdles to the development of mechanistic models that are capable of predicting DMS emission both seasonally and regionally.

Studies of seasonal variations in DMS and DMSP concentrations have played an important part in helping to elucidate some of the important factors controlling DMS emissions. Leck et al. (1990) demonstrated the lack of a relationship between DMS concentrations and phytoplankton biomass or primary production during an annual cycle in the Baltic Sea. They illustrated that variations in DMS concentration must be considered a result of complex physiological and ecological interactions. Studies in both temperate (Kwint & Kramer 1996) and subtropical (Dacey et al. 1998) waters have found that the seasonal trends in DMS concentrations can become decoupled from the temporal changes in DMSP concentrations. Recently, the daily ultraviolet (UV) radiation dose has been shown to statistically explain >77% of the variability in the mixed-layer DMS concentrations in the BATS (Bermuda Atlantic Time-Series Study) data set (Toole & Siegel 2004) and may be a key to understanding the seasonal variations in the ratio of DMS to DMSP. Similarly, the solar radiation dose (SRD), calculated from the full spectrum of surface irradiance and an extinction coefficient for photosynthetically active radiation (PAR, 400 to 700 nm), explained a high proportion of the variance in DMS concentrations measured at BATS (Vallina & Simó 2007).

Why UV radiation and SRD should positively correlate with DMS concentrations in natural waters remains uncertain. High light and, in particular, UV radiation are thought to have an impact on DMS concentrations through a number of opposing processes. Photolysis of DMS can be a substantial removal process (e.g. Kieber et al. 1996) and is primarily driven by UV radiation. UV radiation also has impacts on the bacterial metabolism of DMSP and DMS (Slezak et al. 2001, Toole et al. 2006). Levels of UV radiation appear to affect the degree of intracellular DMSP accumulation in the few phytoplankton taxa that have been tested under laboratory culture conditions. In the prymnesiophyte *Emiliania huxleyi*, cells exposed to short-term (<1 d), elevated levels of UV increased DMSP intracellular concentrations by approximately 20% (Slezak & Herndl 2003) and almost 100% (Sunda et al. 2002), compared to cells exposed to PAR alone. In contrast, exposure to UV at levels sufficiently high to cause unbalanced growth in *E. huxleyi* had no impact on the intracellular concentration of DMSP (Van Rijssel & Buma 2002).

Nutrient availability may also play a role in explaining seasonal and geographic variations in the relative production of DMSP and DMS. Differing nutrient regimes support contrasting phytoplankton communities, which may, in part, explain variations in DMS/chlorophyll *a* (chl *a*) and DMSP/chl *a* ratios between eutrophic and oligotrophic waters (Sunda & Hardison 2008). However, physiological responses of individual taxa of phytoplankton to nutrient availability may have an equally large impact on DMSP and DMS concentrations. Nitrogen limitation caused almost a doubling in intracellular DMSP concentration in *Emiliania huxleyi* and a 30-fold increase in the diatom *Thalassiosira pseudonana* (Keller et al. 1999). Furthermore, under nitrogen-limiting conditions, the potential activity of DMSP-lyase enzymes increased in *E. huxleyi*, possibly explaining a corresponding increase in DMS release from cells compared to a nitrogen-sufficient culture (Sunda et al. 2007).

Increased intracellular DMSP accumulation and DMS production in the face of high light or UV and nutrient limitation are thought to reflect the antioxidant role of DMSP, possibly contributing to the relief of photo-oxidative stress (Sunda et al. 2002). Alternatively, enhanced production of DMSP and DMS under conditions that promote physiological stress may stem from the role of DMSP as a 'secondary metabolite' (Kirst 1996, Stefels 2000). DMSP and its conversion to DMS may act as an overflow mechanism to regulate intracellular sulphur- and nitrogen-containing amino acid proportions or as a means of dissipating excess carbon production (Stefels 2000). There is mounting evidence that DMS release from phytoplankton as a consequence of the physiological role(s) of DMSP and DMS may make a substantial contribution to DMS production in natural waters (Archer 2007). In a seasonal study in the north-western Mediterranean, increased yields of DMS production from DMSP during the summer months were attributed to physiological release from phytoplankton (Vila-Costa et al. 2008). However, a clear understanding and direct physiological evidence for either the putative antioxidant role or for the proposed metabolic overflow mechanism are lacking.

One approach to understanding the roles of DMSP and DMS is to compare their production rates to those of compounds with well-defined physiological roles. Phytoplankton possess a variety of strategies to accommodate the conflicting requirements of absorbing adequate radiation to drive photosynthesis in a highly variable light and nutrient environment and the potentially harmful effects of absorbing too much radiation, which may lead to production of reactive oxygen spe-

cies (ROS). Excess energy absorbed by light harvesting complexes may be dissipated through the reactions of the xanthophyll cycle pigments, in order to prevent photoinhibition and ROS formation. The major groups of eukaryotic phytoplankton convert the mono-epoxide xanthophyll pigment diadinoxanthin (Dd) to a de-epoxide form, diatoxanthin (Dt), as a mechanism to dissipate excess energy (Arsalane et al. 1994). High levels of UV radiation in near-surface waters may exacerbate ROS production by preventing the utilisation of electrons generated through photosynthesis by damaging enzymes of the electron transfer chain and the reaction centre in Photosystem II and through damage to DNA and RNA (reviewed in Davidson 2006). As one of a range of strategies to prevent UV damage, phytoplankton synthesise UV-absorbing compounds, consisting primarily of mycosporine-like amino acids (MAAs) (Hannach & Sigleo 1998, Neale et al. 1998).

The current study presents a high temporal resolution, seasonal study of the DMS and DMSP concentrations in temperate shelf seas. The study site is characterised by a high degree of variability in physical forcing and biological productivity throughout the year and by a relatively consistent pattern of phytoplankton taxonomic succession (Holligan & Harbour 1977). In order to improve understanding of the functional roles of DMSP and DMS, the present study aimed to: (1) determine the extent and patterns of seasonal variation in DMS and DMSP concentrations, in relation to changing physico-chemical forcing; (2) determine how these concentrations vary in relation to phytoplankton abundance and taxonomy; and (3) compare the seasonal patterns of DMSP and DMS with the concentrations of photoprotective xanthophyll cycle pigments and UV-absorbing MAAs, in relation to irradiance levels.

MATERIALS AND METHODS

Time-series site and sampling. Long-term, weekly monitoring of a range of physical, chemical and biological parameters has been carried out at Station (Stn) L4 since 1988 (www.pml.ac.uk/ L4). Stn L4 is located in the western English Channel, at 50° 15′ N, 04° 13′ W, 10 km offshore and in approximately 55 m of water (Fig. 1). Sampling was carried out at approximately weekly intervals from March 2003 to April 2004, weather permitting. As part of the long-term monitoring programme at L4, single samples were routinely collected at 10 m depth in a 10 l Niskin bottle for nutrient analysis, pigment concentrations, MAA concentrations and phytoplankton abundance. As the mixed-layer depth (MLD) is generally deeper than 10 m at Stn L4, including on all dates in the present study, all samples were considered to be from the upper mixed layer.

Water column characteristics. A part of the regular Stn L4 sampling programme included deployment of an optical rig on which a Sea Bird 19+ CTD (Serial Numbers: 4180 and 4307) was mounted. A fast repetition rate fluorometer (FRRF; Chelsea Technologies Ltd. FAST*tracka*) was deployed horizontally on the top of the optics rig with a depth sensor and a 2π PAR sensor (400 to 700 nm).

Nutrient concentrations were determined in samples that were frozen at –20°C and stored for later analysis. Nitrate and phosphate concentrations were determined by colorimetric auto-analysis (Woodward & Rees 2001), with detection limits of 0.05 and 0.02 µM, respectively.

DMSP and DMS concentrations. Seawater was collected from the surface using a stainless steel bucket and from 10 m using a 10 l Niskin bottle on a rosette sampler. Samples were stored in the dark in acid-

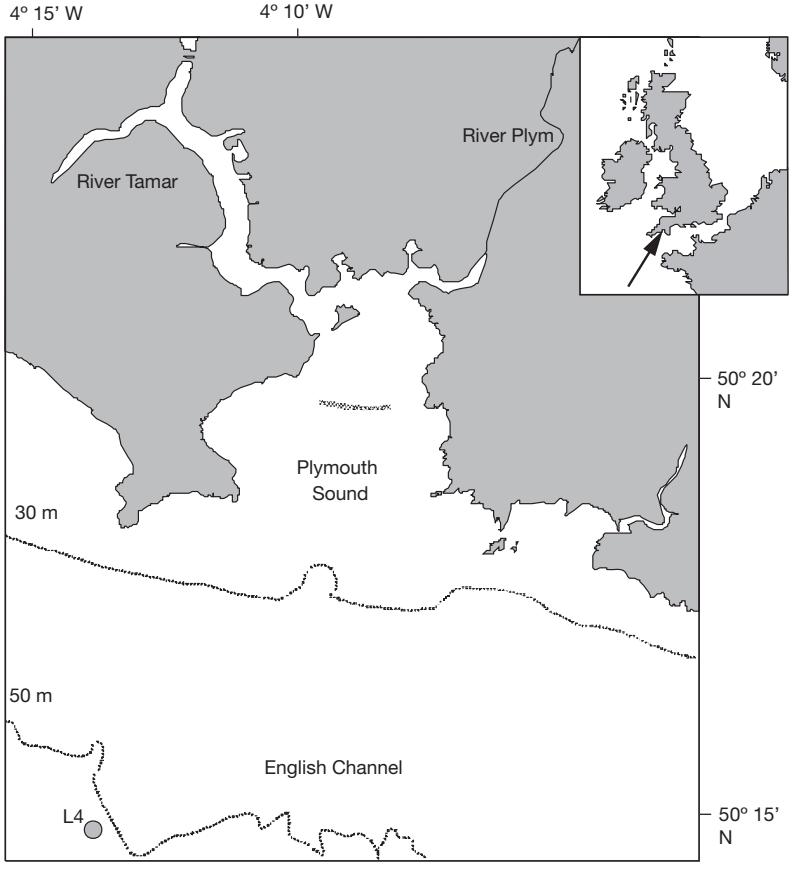

Fig. 1. Location of the time-series sampling station (Stn L4)

cleaned glass bottles sealed with ground glass stoppers with no headspace. The bottles were kept in a cool box through which seawater at ambient temperature was pumped and were processed immediately on returning to the laboratory within 2 h of collection. A cryogenic purge-and-trap/gas chromatography system was used to determine DMS and DMSP concentrations. In order to measure DMS concentrations, 10 ml samples were gravity filtered through a 25 mm GF/F filter into a narrow glass vial avoiding any droplet formation, and 5 ml was immediately transferred from the bottom of the vial to a purge tower in order to reduce potential gas exchange. To quantify DMS concentrations, the filtrate was sparged in a stream of nitrogen and the purge gas trapped at –160°C in a Teflon loop. The filter and sparged filtrate were retained for determination of particulate DMSP and dissolved DMSP concentrations following alkaline hydrolysis to DMS in sealed glass vials in 0.5 M NaOH. Recent evidence indicates that even when gentle filtration techniques are used, leakage of DMSP from cells is likely to occur (Kiene & Slezak 2006). In order to provide a more accurate measurement, the dissolved and particulate DMSP concentrations determined from each filtered sample are presented as a combined total DMSP concentration (DMSPt). A Varian 3800 gas chromatograph equipped with a pulsed flame photometric detector (PFPD) and a Varian 30 m × 0.53 mm CP Sil 5CB column was used to analyse the trapped gas. DMS standards for calibration were prepared from DMSP-HCl (>98% purity, CASS, University of Groningen) in a 0.5 M NaOH solution in Milli-Q water. For this system, analytical precision (% SD) is typically better than 5% for DMS and DMSP standards. Analytical error and sample variability were tested on occasion by collecting 3 samples from the same depth. For instance, the coefficients of variation, which incorporated both analytical error and sample difference, for 3 samples collected from the same depth on 12 and 19 May 2003, were 7.1 and 7.5% for DMS and 2.1 and 2.3% for DMSPt.

Pigment and MAA concentrations. Pigment and MAA concentrations were determined in 1 l volumes that were separately vacuum filtered to retain phytoplankton on 25 mm GF/F filters, which were stored in liquid N_2 until analysis. Pigments were extracted from filtered phytoplankton into 2 ml acetone using an ultrasonic probe (30 s, 50 W). An internal standard of apo-carotenoate (Sigma-Aldrich Company Ltd.) was added to the acetone. Extracts were centrifuged to remove filter and cell debris (5 min at 20 × *g*), and pigments were separated by injection onto a reversed-phase column (Hypersil 3 mm C8 MOS-2) with gradient elution, linked to a high-performance liquid chromotograph (HPLC) with a photodiode array (PDA) detector (Agilent 1100 system). Pigments were identified using retention time and spectral matching by PDA detector (Jeffrey et al. 1997), and concentrations were calculated from calibrations using a suite of standards (DHI Water and Environment).

MAAs were extracted from filtered phytoplankton into 2 ml methanol by sonication with an ultrasonic probe (35 s, 50 W). The extracts were incubated at 45°C for 2 h (Tartarotti & Sommaruga 2002) and then centrifuged (5 min at 20 × *g*) to remove cellular debris. The supernatant was injected (100 µl) into a HPLC with a Luna (Phenomenex) 5 µm NH_2 column (250 × 4.6 mm). Mobile Phase A comprised 85% acetonitrile (15% 1 M ammonium carbonate buffered to pH 10), and Mobile Phase B comprised 75% 1 M ammonium carbonate and 25% acetonitrile. Each mobile phase was pre-mixed and degassed by gently bubbling with N_2 gas for 10 min. The gradient programme was: 100% A for 10 min and then a linear gradient to 75% B and 25% A over 35 min at a flow rate of 1 ml min^{-1}. MAAs were monitored at 330 and 310 nm using a PDA detector, scanning between 250 and 500 nm. For quantification, pure samples of palythene, shinorine, mycosporine-glycine, palythine and palythinol, previously isolated from culture extracts by preparative HPLC and verified by liquid-chromatography–mass spectrometry, were quantified using published extinction coefficients (Grönginer et al. 2000) and subsequently analysed by analytical HPLC to establish response factors. The response factors were then used to quantify the MAAs in sample extracts.

Phytoplankton abundance. Flow cytometry was used to enumerate nanophytoplankton (2 to 20 µm in size) in unfixed samples. Flow cytograms of 90° light scatter, red and orange fluorescence were used to distinguish and enumerate the single cells of the nanophytoplankton population. Larger phytoplankton were identified and enumerated in samples fixed with Lugol's solution using inverted-microscopy techniques (see www.pml.ac.uk/L4 for details).

Irradiance and radiation dose calculations. Surface irradiance was recorded at the ELDONET station (www.eldonet.org) at the University of Plymouth (50° 30′ N, 04° 10′ W). The 3-channel dosimeter provided data for UVB (280 to 315 nm), UVA (315 to 400 nm) and visible radiation (PAR, 400 to 700 nm). Sample collection at Stn L4 occurred between 10:00 and 11:00 h, and the radiation dose was calculated from the 24 h irradiance data for the date of sampling. Original irradiance data, averaged every minute, were used to calculate an average surface value (W m^{-2}) for each 24 h period.

Depth-dependent PAR was estimated from the daily average surface value using a diffuse attenuation coefficient for downwelling irradiance (K_d) calculated from the directly measured water-column profile for PAR at each

sampling time. The average mixed-layer downwelling radiation dose for PAR was determined from depth-dependent light estimates and the MLD, defined as the point at which a 0.8°C difference from the sea surface temperature occurred (Kara et al. 2000).

RESULTS

Environmental variables at Stn L4

Stn L4 experiences a climate typical of northern temperate waters with more than a 30-fold variation in the average daily solar radiation at the surface between mid-summer and mid-winter months and high daily variability as a result of cloud cover. Near-surface water temperatures did not start to rise above winter levels of 8 to 9°C until early May and reached a maximum of approximately 18°C in August (Fig. 2A). The water column at L4 shows some stabilisation as water temperatures rise, and varying degrees of stratification occur during the summer months and from year to year. A relatively long period of water column stability occurred during the summer of 2003, with consistent stratification and a MLD of between 10 and 23 m that lasted from late-May to mid-August (Fig. 2A).

Formation of a mixed layer intensified the levels of PAR experienced by near-surface phytoplankton during summer months (Fig. 2B). Furthermore, when the water column was stabilised, not only were PAR doses elevated, but the relative dose of UVB received by the phytoplankton was likely to have been higher, as indicated by the increased ratio of surface UVB to PAR irradiance (Fig. 2B).

In conjunction with water column stability, nutrient concentrations varied markedly during the year. Nitrate concentrations began to decrease in mid-February from typical winter values of from 7 to 12 µmol l^{-1} to values below the detection limit of 0.05 µmol l^{-1} by mid-May and remained at low nanomolar concentrations until late-August (Fig. 2C). Phosphate concentrations showed a similar pattern, although concentrations remained relatively high (>0.4 µmol l^{-1}) until early May, when they dropped to values of ~0.1 µmol l^{-1}, typical of the stratified summer conditions at L4 (Fig. 2C). Concentrations recovered dramatically to >0.4 µmol l^{-1} again, once the water column stability broke down in mid-August.

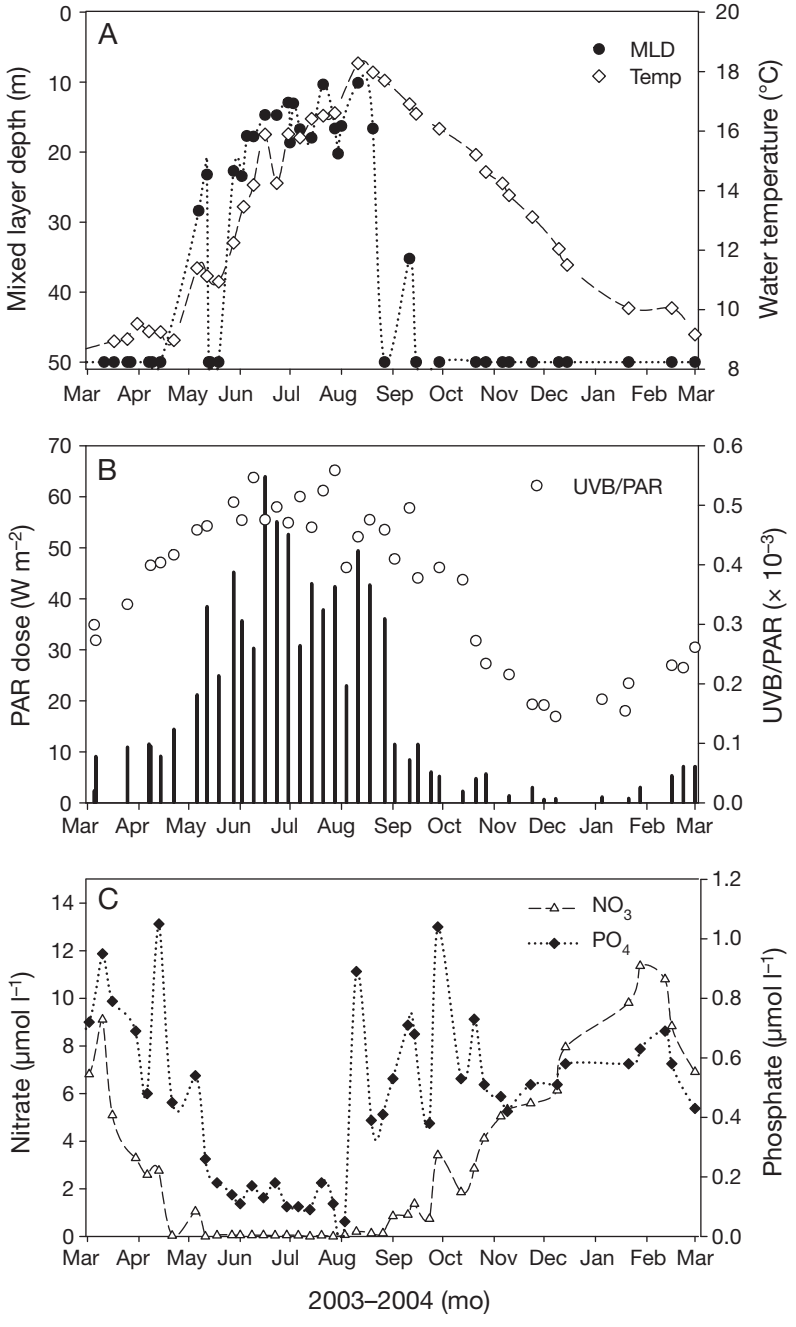

Fig. 2. The physico-chemical environment at Stn L4 during the study period. (A) Mixed layer depth (MLD) calculated according to Kara et al. (2000) and seawater temperature measured at 2 m. (B) Daily average mixed layer PAR dose and the ratio of surface UVB/PAR (ultraviolet-B to photosynthetically active radiation) irradiance, calculated on each sampling day at L4. (C) Con-centrations of nitrate and phosphate measured in samples from 10 m

DMS and DMSP concentrations

Near-surface concentrations of DMSPt ranged from as low as 3 nmol l^{-1} during winter months to a maximum of 127 nmol l^{-1} in mid-August (Fig. 3A). An obvious seasonal pattern in the DMSPt concentrations was apparent during the 2003 to 2004 study, which appeared to coincide with the trend in solar radiation and the stability of the water column. An almost continuous increase in DMSPt occurred from late-March through to July. Concentrations remained high during July and August, before they dropped rapidly between late-August and early-September, as stratification of the water column broke down (Fig. 3A).

Average concentrations of DMS in the top 10 m ranged from <0.1 nmol l^{-1} in mid-winter to 23 nmol l^{-1} during June 2003 (Fig. 3B). Two periods of high DMS concentration were obvious in the seasonal pattern, the first from late-March to early-May and the second during June. Outside of these periods, even in late summer when DMSPt concentrations were high, DMS concentrations remained <5 nmol l^{-1}. The 2 peaks in DMS concentration are clear in the seasonal pattern of the DMS/DMSPt ratio, emphasising that elevated DMS concentrations were not simply a product of higher levels of DMSPt (Fig. 3C).

Phytoplankton cell constituents and taxonomy

As is typical in these waters, the highest chl *a* concentrations occurred over a short period in spring, reaching 5.5 µg l^{-1} in mid-April 2003 (Fig. 4A). During the winter months chl *a* concentrations varied between 0.5 and 1.0 µg l^{-1}. Summer and autumn were characterised by variable concentrations between 1.0 and 3.0 µg l^{-1}, although the lowest of all of the concentrations (0.1 µg l^{-1}) was measured during a period from late-May to early-June, which coincided with the onset of stratification. The ratio of DMSPt (FW 135) to chl *a*, a proxy for the accumulation of intracellular DMSP relative to light-harvesting capacity, varied seasonally by >40-fold, from 0.4 to 27.5 g g^{-1}, with the highest values in the mixed layer during summer months (Fig. 4B). Peridinin, a specific marker pigment for Type 1 Dinophyta (Jeffrey & Wright 2006), varied between undetectable concentrations and 120 ng l^{-1} (data not shown). The peridinin to chl *a* ratio was highly variable, ranging from 0 to 0.17 g g^{-1}, and showed a similar seasonal trend to that of DMSPt/chl *a*, with highest values during summer months when the water column was stratified and 2 distinct peaks in June and August (Fig. 4B). 19-hexanoyloxyfucoxanthin (19-Hex) is regarded as a marker pigment for Haptophyta, including the DMSP-rich taxa *Phaeocystis* spp. and *Emiliania huxleyi*, and for some Dinophyta. Concentrations of 19-Hex ranged between 10 and 350 ng l^{-1}, and the 19-Hex to chl *a* ratio varied between 0.004 and 0.26 (data not shown). However, the seasonal pattern of 19-Hex/chl *a* showed little similarity to that of DMSP/chl *a* (Table 1).

The combined concentrations of the xanthophyll pigments Dd and Dt varied throughout the year from 8 to 290 ng l^{-1}. When normalised to chl *a*, the ratio [(Dd +

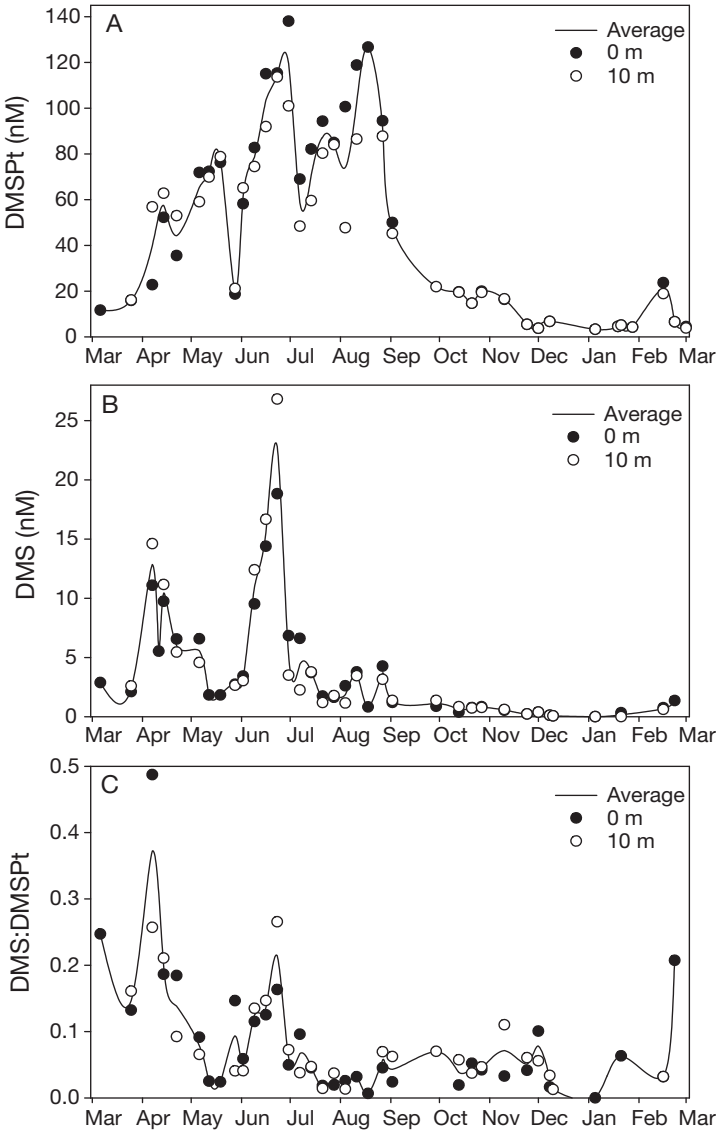

Fig. 3. Seasonal variations in: (A) DMSPt (total β-dimethylsulphoniopropionate) and (B) DMS (dimethyl sulphide) concentrations measured in the upper 10 m of the water column at Stn L4. (C) Average molar ratio of DMS/DMSPt. Values were taken from the surface and 10 m; the line illustrates the average value or the surface value when it was not possible to obtain a 10 m sample

Dt)/chl *a*] varied almost 10-fold between the minimum in October of 0.025 g g^{-1} and a summer maximum in July of 0.228 g g^{-1} (Fig. 4C). In broad terms, the seasonal trend in Dd + Dt resembled that of chl *a*, but with generally reduced xanthophyll cycle pigment concentrations relative to chl *a* in spring and autumn compared to the period of maximum irradiance in summer (Fig. 4C).

MAAs were present throughout the 2003 to 2004 study period at L4, and their combined concentrations showed a similar seasonal pattern to that observed in 1998 (Llewellyn & Harbour 2003). The total quantified MAA concentrations varied from 1 to 350 ng l^{-1} and were dominated by shinorine, mycosporine glycine and porphyra-334, with additional contributions from palythenic acid, palythene, palithine and an unidentified compound. The MAA/chl *a* ratio varied >20-fold, remaining below 0.01 g g^{-1} from the end of August to the end of March, whilst values >0.05 g g^{-1} were restricted to June and early July and a peak in August (Fig. 4C).

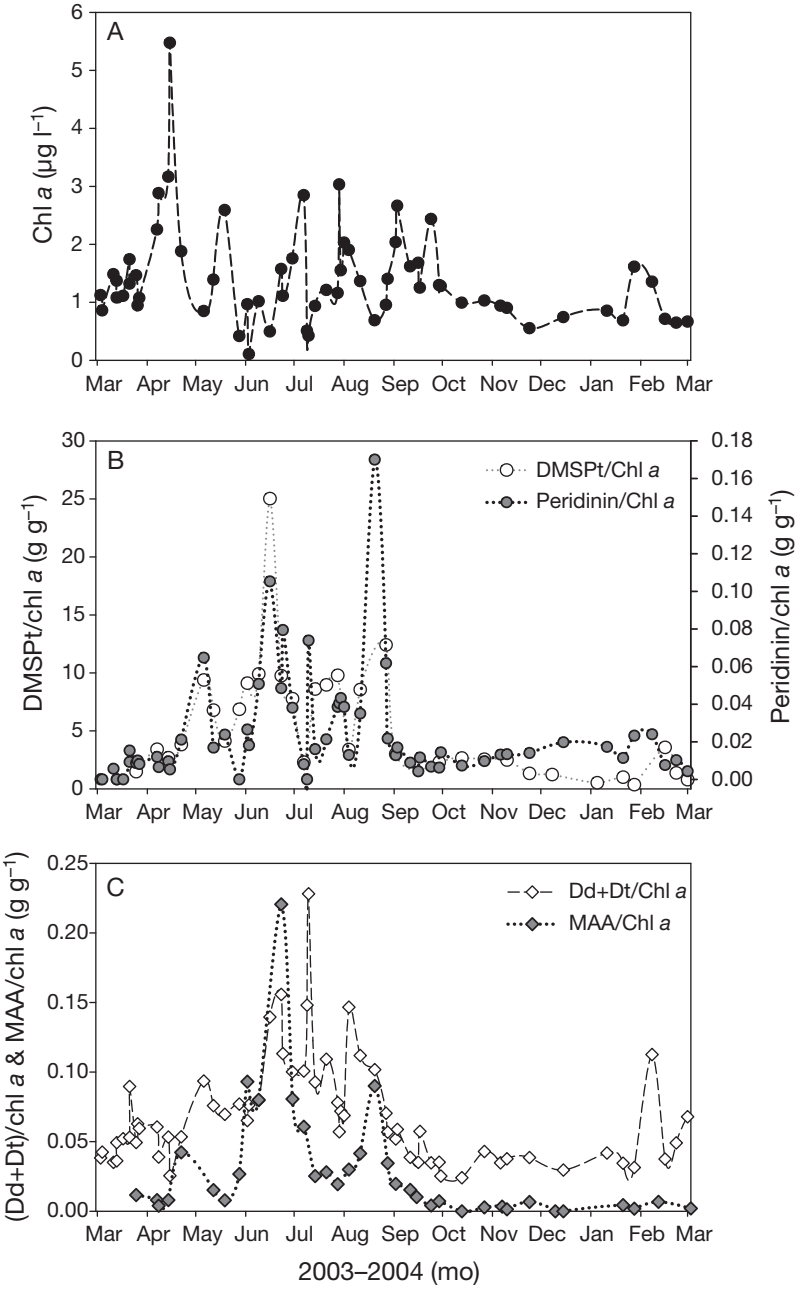

Fig. 4. Seasonal variations at Stn L4 in: (A) chlorophyll *a* (chl *a*) concentration, (B) DMSPt measured at 10 m to chl *a* and peridinin to chl *a*. (C) Ratios of the combined xanthophyll cycle pigments diadinoxanthin (Dd) and diatoxanthin (Dt) to chl *a* and micosporine-like amino acids (MAA) to chl *a*

Contributors to DMSP standing stocks

Chl *a* and DMSPt showed no significant relationship, suggesting that as seasonal taxonomic succession occurred, the relative investment in chlorophyll *a* and DMSP accumulation altered (Table 1). An indication of the components of the phytoplankton communities responsible for DMSP production can be gained from the combination of phytoplankton abundance (www.pml.ac.uk/L4) and the concentrations of marker pigments. Nanophytoplankton abundance showed a similar seasonal pattern and significant relationship to DMSPt (Fig. 5A, B, Table 1), suggesting this component of the phytoplankton contributed substantially to DMSP production. In common with other years, *Phaeocystis pouchetii* occurred in relatively high abundance from mid-March to late April in the western English Channel. Based on a cell content of 2 pg DMSP $cell^{-1}$ for *P. globosa* (Stefels & van Boekel 1993) and assuming similar DMSP cell content in the 2 species, *P. pouchetii* accounted for an estimated 40 to 60 nmol l^{-1} DMSPt during this time (Fig. 6A). This contribution by *P. pouchetii* may be an underestimate, as the low volumes analysed for flow cytometric cell counting are likely to underestimate the abundance of colonial *P. pouchetii* cells, possibly explaining the difference between derived and observed DMSPt concentrations. Lithed *Emiliania huxleyi* occurred sporadically throughout the summer months, but at low concentrations of ≤250 cells ml^{-1}. At these abundances, *E. huxleyi* would contribute <2 nmol DMSPt l^{-1}, assuming a cell content of 1 pg DMSP $cell^{-1}$ (Keller et al. 1989). It is possible that non-lithed life stages of *E. huxleyi* were more abundant, but were not possible

Table 1. Least-squares, linear regression analyses ($y = ax + b$) between seasonally varying parameters measured at Stn L4; for nitrate and phosphate, $y = a\ln(x) + b$. Values of the relationships shown in Figs. 5 to 8 are included. p: the level of significance in the analysis of variance; NS: value not significant, $p > 0.05$; superscript a: the average value of measurements at 0 and 10 m; superscript b: the value measured at 10 m; DMSPt: total β-dimethylsulphoniopropionate; DMS: dimethyl sulphide; Dd + Dt: diadinoxanthin + diatoxanthin; MAA: mycosporine-like amino acids; PAR: photosynthetically active radiation

	a	*b*	r^2	p
Water temperature (°C)				
DMSPt (nmol l^{-1})[a]	7.5 ± 1.9	NS	0.35	0.0006
DMS (nmol l^{-1})[a]	NS	NS	0.00	0.83
DMSPt/chl *a* (g g^{-1})[b]	0.72 ± 0.30	NS	0.17	0.025
Chlorophyll *a* (ng l^{-1})[b]				
DMSPt (ng l^{-1})[b]	NS	NS	0.12	0.06
DMS (ng l^{-1})[b]	NS	NS	0.06	0.22
Dd + Dt (ng l^{-1})[b]	0.042 ± 0.007	30 ± 12	0.36	<0.0001
MAA (ng l^{-1})[b]	0.019 ± 0.009	NS	0.12	0.04
DMSPt (ng l^{-1})[b]				
Dd + Dt (ng l^{-1})[b]	0.009 ± 0.002	37 ± 8	0.37	0.0001
MAA (ng l^{-1})[b]	0.010 ± 0.003	NS	0.39	0.0002
Nanophytoplankton (cells ml^{-1})[a]				
DMSPt (pg ml^{-1})[a] (Fig. 5)	2.7 ± 0.4	1520 ± 780	0.67	<0.0001
Peridinin (ng l^{-1})[b]				
DMSPt (ng l^{-1})[b] (Fig. 6)	186 ± 22	1030 ± 790	0.71	<0.0001
Dd + Dt (ng l^{-1})[b]	1.10 ± 0.24	58 ± 9	0.25	0.001
MAA (ng l^{-1})[b]	0.17 ± 0.07	NS	0.16	0.018
19-Hexanoyloxyfucoxanthin (ng l^{-1})[b]				
DMSPt (ng l^{-1})[b]	30 ± 9	NS	0.25	0.003
PAR dose (W m^{-2})				
DMSPt/chl *a* (g g^{-1})[b] (Fig. 7)	0.21 ± 0.03	NS	0.68	<0.0001
DMS (nmol l^{-1})[a] (Fig. 7)	0.13 ± 0.04	NS	0.25	0.002
DMS/DMSPt (mol mol^{-1})[a]	NS	0.11	0.01	0.60
(Dt + Dd)/chl *a* (g g^{-1})[b] (Fig. 7)	0.0015 ± 0.0002	0.037 ± 0.005	0.66	<0.0001
MAA/chl *a* (g g^{-1})[b] (Fig. 7)	0.0017 ± 0.0003	NS	0.47	<0.0001
Peridinin/chl *a* (g g^{-1})[b]	0.0066 ± 0.0028	NS	0.15	0.02
Nitrate (μM)[b]				
Ln(DMSPt/chl a) (g g^{-1})[b] (Fig. 8)	−0.23 ± 0.03	1.9 ± 0.1	0.64	<0.0001
Ln(DMS) (nmol l^{-1})[b]	−0.38 ± 0.08	1.5 ± 0.3	0.49	<0.0001
Ln(DMS/DMSPt) (mol mol^{-1})[b]	NS	NS	0.00	0.39
Ln[(Dd + Dt)/chl a] (mg g^{-1})[b]	−0.12 ± 0.02	11.5 ± 0.1	0.26	0.0005
Ln(Peridinin/chl *a*) (mg g^{-1})[b]	−0.11 ± 0.05	3.0 ± 0.2	0.12	0.03
Phosphate (μM)[b]				
Ln(DMSPt/chl a) (g g^{-1})[b]	−1.61± 0.001	2.0 ± 0.3	0.22	<0.008
Ln(DMS) (nmol l^{-1})[b]	NS	NS	0.04	0.30

to discriminate from the general nanophytoplankton population. However, there was only a marginally significant relationship between DMSPt and 19-Hex on a seasonal basis (Table 1).

In contrast, concentrations of peridinin explained 71% of the variability in DMSPt concentrations (Fig. 6B, Table 1). Abundant dinoflagellate taxa that were identified included *Karenia mikimotoi*, which occurred at highest concentrations of ~100 cells ml^{-1} during a 2 wk period in late June to early July. Although this coincided with a peak in DMSPt (Fig. 6), measured intracellular concentrations of *K. mikimotoi* (= *Gyrodinium aureolum*) are low (<1 pg DMSP $cell^{-1}$) amongst the Dinophyta (Keller et al. 1989). On the other hand, the dinoflagellate *Scrippsiella trochoidea*, which occurred at abundances approaching 25 cells ml^{-1} and may contain as much as 380 pg DMSP $cell^{-1}$ (Keller et al. 1989), may have contributed to the bulk of the DMSPt at this time (Fig. 6). The DMSP-rich dinoflagellate *Prorocentrum minimum* occurred at concentrations reaching 500 cells ml^{-1} during August and, based on a cell content of 20 pg DMSP $cell^{-1}$ (Keller et al. 1989), may have made up the major part (~60%) of the peak in DMSPt at that time (Fig. 6). The strong relationships between DMSPt, nanophytoplankton abundance and peridinin, but not 19-Hex, suggest that a significant proportion of the nanophytoplankton were dinoflagellate taxa that were not specifically identified in the microscope analyses, possibly due to their small size.

Environmental forcing and physiological function

Temperature explained approximately 30% of the variability in average DMSPt concentrations and the DMSP/chl *a* ratio in the upper 10 m at L4 from 2003 to 2004 (Table 1). DMS concentrations showed no significant relationship to water temperature.

DMSPt/chl *a* was considerably more sensitive to seasonal changes in the light environment experienced by the phytoplankton community at L4, showing a highly significant relationship ($r^2 = 0.68$, $p < 0.0001$) to PAR dose (Fig. 7A, Table 1). DMS concentrations also showed a significant relationship to PAR dose, but at a lower level of significance than that observed for DMSPt/chl *a* (Fig. 7B, Table 1).

That the relationship between DMSPt/chl *a* and PAR dose is linked photophysiologically to the role of DMSP is supported by the similar level of significance seen between (Dt + Dd)/chl *a* and PAR dose and between MAA/chl *a* and PAR dose (Fig. 7C, D, Table 1).

Although DMSPt/chl *a*, (Dd + Dt)/chl *a* and MAA/chl *a* were clearly closely related to PAR dose (Fig. 7), DMSPt concentrations explained only 37 and 39% of the variability in Dd + Dt and MAA concentrations (Table 1). This may be a product of the high variability in all 3 parameters during the months when water column stratification occurred, illustrated in the chl *a*–normalised concentrations (Fig. 4).

Nitrate concentrations showed a non-linear, inverse relationship to DMSP/chl *a* and DMS with particularly high variability in DMSP/chl *a* at the lowest nitrate concentrations (Fig. 8) that coincided with stratification of the water column. Taking into account this high variability at low concentrations, nitrate explained 64 and 49% of the variability in log-transformed DMSP/chl *a* ratios and DMS concentrations, respectively (Fig. 8, Table 1). More accurate measurements of nitrate concentrations below the detection limit of 0.05 µM may have increased the significance of these relationships. Less significant relationships occurred between nitrate concentrations and log-transformed (Dd + Dt)/chl *a* or peridinin/chl *a* ratios (Table 1). Phosphate concentrations provided a weaker explanation (22%) of seasonal variations in log-transformed DMSP/chl *a* ratios and showed no significant relationships to DMS concentrations (Table 1).

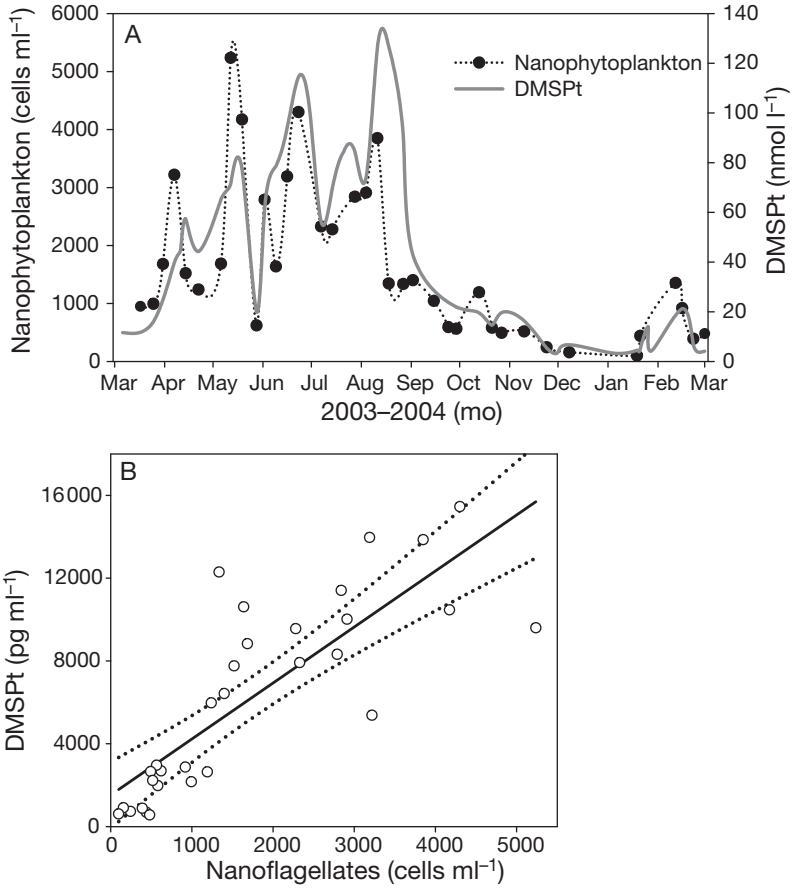

Fig. 5. (A) Seasonal variation at Stn L4 in the abundance of nanophytoplankton quantified by flow cytometry in relation to average DMSPt concentrations. (B) Relationship between nanophytoplankton abundance and DMSPt concentration. The values shown are the average of surface and 10 m samples

DISCUSSION

Although seasonal uncoupling between phytoplankton biomass and DMSP and between DMSP and DMS concentrations are considered to be widespread features globally (e.g. Simó & Pedrós-Alió 1999), these assumptions are based on relatively few comprehensive seasonal observations. The present study illustrates that at a relatively productive, temperate shelf location, DMSP/chl *a* ratios can vary seasonally by 40-fold (Fig. 4) and that DMS/DMSP ratios are highly variable, with elevated relative DMS concentrations during spring and mid-summer (Fig. 3). In contrast, DMSP and DMS concentrations were very closely related from May to November in near-shore waters of the Saint Lawrence Estuary, which is located at similar latitude to the western English Channel (Michaud et al. 2007). The difference between these 2 sites may reflect the impact that the seasonal stratification and resulting elevated irradiance levels that occur at Stn L4 has on phytoplankton physiology, in contrast to the more tidally mixed, near-shore environment of the Saint Lawrence Estuary. Similar degrees of uncoupling between DMSP and chl *a* and between DMSP and DMS to those found in the present study were observed in the seasonal cycle conducted in the oligotrophic Sargasso Sea at BATS (Dacey et al. 1998, Lefèvre et al. 2002). However, the degree to which PAR dose explains the variability in DMS concentrations in the western English Channel (31%; Table 1) is considerably lower than observed for the relationship between DMS and UV radiation dose (77%) or monthly average DMS verses solar radiation dose (81%) at BATS (Toole & Siegel 2004, Vallina & Simó 2007).

Seasonal uncoupling of DMS from DMSP concentrations in the western English Channel, evident as variations in DMS/DMSP (Fig. 3), appears to be partly a consequence of taxonomic succession of eukaryotic phytoplankton. The highly significant relationship between peridinin and DMSPt and the apparently major contribution to the highest peaks in DMSPt concentrations during the year made by *Scrippsiella tro-*

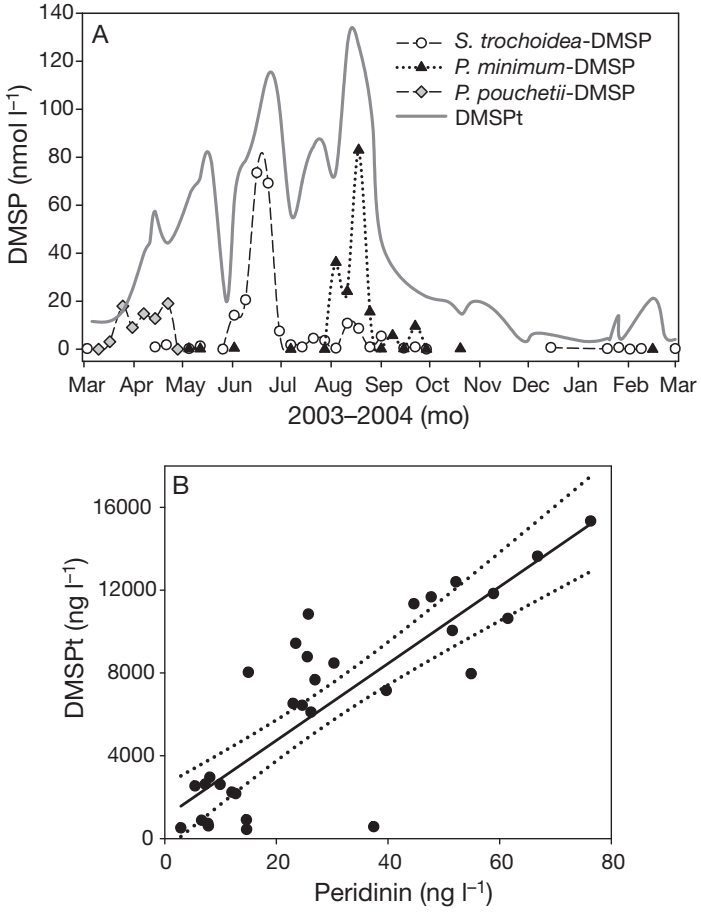

Fig. 6. (A) Contribution of 3 individual taxa (*Scrippsiella trochoidea*, *Prorocentrum minimum*, *Phaeocystis pouchetii*) to DMSPt concentrations in the upper 10 m at Stn L4. The contribution of each taxon was estimated from cell abundance measured in samples from 10 m depth and literature values of the DMSP cell content (see 'Results' for details). (B) Relationship between concentrations of peridinin, the marker pigment for Type 1 dinoflagellates, and DMSPt in the upper 10 m at Stn L4

choidea and *Prorocentrum minimum* (Fig. 6, Table 1) illustrate the important role that Dinophyta play in DMSP production in this temperate shelf location. However, caution should be applied when estimating the contribution of specific taxa based on literature values of cellular DMSP, as intracellular concentrations have been shown to vary in culture in relation to the nutrient and light environment (Stefels et al. 2007). Despite similar DMSP concentrations attributed to *S. trochoidea* and *P. minimum*, substantially higher concentrations of DMS occurred during June/July when *S. trochoidea* was relatively abundant compared to the period in August when *P. minimum* appeared to dominate DMSP production (Fig. 3). Why so much lower DMS concentrations resulted from DMSP production by *P. minimum* is unclear. Levels of irradiance were similar, and the water column remained stratified

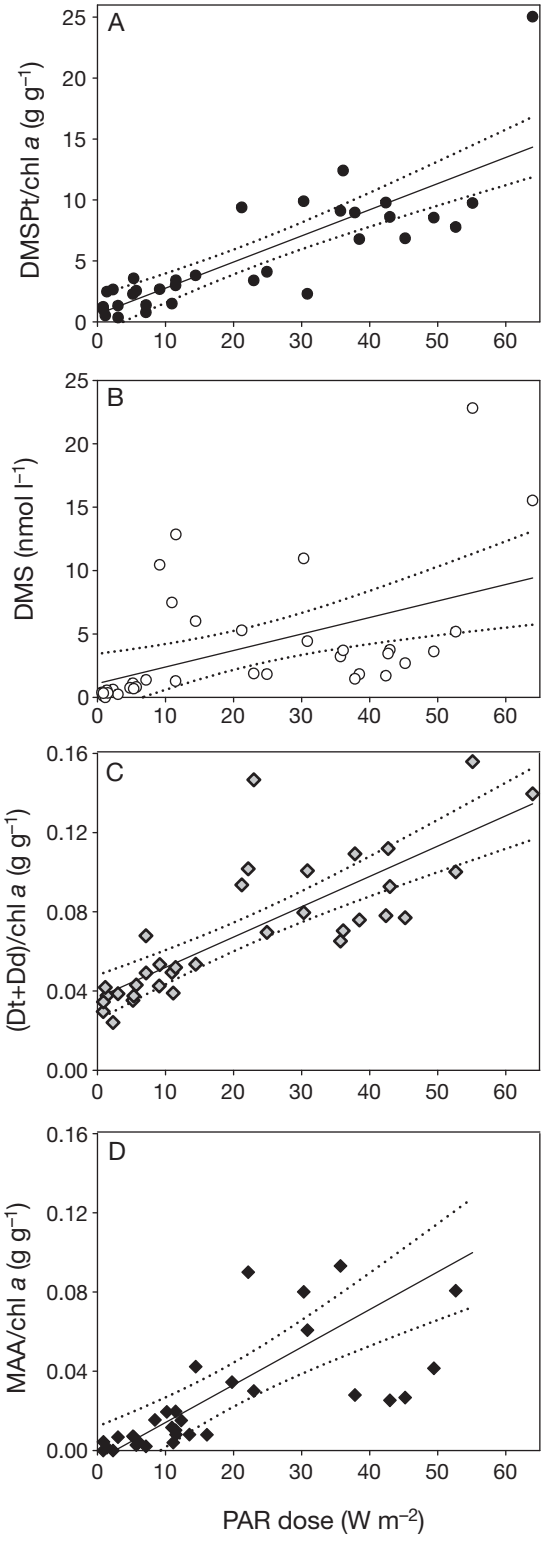

Fig. 7. Relationship between the daily average doses of photosynthetically active radiation (PAR) and (A) DMSPt/chl *a*, (B) DMS, (C) (Dd + Dt)/chl *a* and (D) MAA/chl *a* at Stn L4 during the study period. Details of the linear regressions are given in Table 1. Dotted lines are the 95% confidence limits

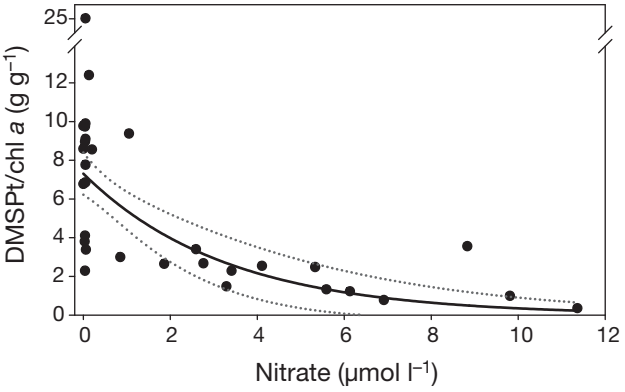

Fig. 8. Relationship between nitrate concentration and DMSP/chl *a* at Stn L4 during the study period. A logarithmic fit to the data is shown, the details of which are given in Table 1. Dotted lines are the 95% confidence limit

during the occurrence of both species. It is possible that the heterotrophic community may have had differing degrees of requirement for DMSP and DMS, with greater metabolic utilisation of DMS in August, resulting in the low DMS/DMSPt ratio. Alternatively, the 2 dinoflagellate species may utilise DMSP for different physiological functions. *S. trochoidea* was found to convert dissolved DMSP to DMS at a high rate, suggesting it possesses an active DMSP-lyase capability (Niki et al. 2000), which may account, in part, for the higher DMS concentrations observed in June. Certainly the spring peak in DMSPt concentrations combined with a high DMS/ DMSPt ratio is characteristic of *Phaeocystis* spp. and may reflect the highly active, extracellular DMSP-lyase that these species seem to possess (Stefels & van Boeckel 1993). Interestingly, *Karenia mikimotoi* co-occurred with *S. trochoidea* and at higher abundances, but is considered to be a low producer of DMSP (Keller et al. 1989). Further study of why these 3 dinoflagellate species differ and, in the case of *K. mikimotoi*, whether an alternative strategy to DMSP production occurs may shed more light on the physiological functions of DMSP and its breakdown products.

Mechanistic models that incorporate radiation effects on the parameterisation of DMS cycling processes have shown improved skill at simulating the seasonal patterns of DMS concentrations for the BATS time series (Lefèvre et al. 2002, Toole et al. 2008,Vallina et al. 2008). In both more recent models, the incorporation of a DMS production pathway dependent on UV-driven (Toole et al. 2008) or solar-radiation-driven (Vallina et al. 2008) release of DMS from phytoplankton appeared to be the most important contributing parameterisation to improved simulation of the observed seasonal data set. Justification for the inclusion of light-driven DMS release from phytoplankton in these models stems primarily from evidence that DMSP and its breakdown products may act as antioxidants in phytoplankton (Sunda et al. 2002). The increase in DMSPt/chl *a* in the face of increased PAR dose and possibly elevated UVB exposure at L4 are consistent with intracellular up-regulation of an antioxidant system in the face of environmental stress and/or selection of algal taxa or strains possessing high intracellular DMSP to minimise levels of oxidative stress. The highly significant relationship between DMSPt/chl *a* and light levels (Table 1) suggests that a photophysiological function influences the seasonal cycle of DMSP in temperate waters.

The indirect evidence that DMSP has a photophysiological role is strengthened by the observations that the accumulation of photoprotective and UV-absorbing compounds showed a similar response to seasonally varying light fields. The significant relationship between the chlorophyll-specific xanthophyll pigment pool [(Dd + Dt)/chl *a*] and PAR dose (Fig. 7) illustrates an adaptive requirement for greater capacity to prevent photoinhibition amongst the phytoplankton communities that inhabited the high-irradiance, stratified waters during summer months. Although it is possible that variation in (Dd + Dt)/chl *a* may reflect taxonomic succession, diadinoxanthin and diatoxanthin are synthesised by a high proportion of the microalgal taxa that dominate the phytoplankton communities at L4, including members of the Bacillariophyta, Haptophyta and Dinophyta (reviewed in Jeffrey & Wright 2006). Despite the energetically efficient mechanism of recycling of Dt to Dd following de-epoxidation, an increase of the intracellular concentration of xanthophyll pigments appears to be a common longer term response to prevent photoinhibition. Higher intracellular concentrations of the xanthophyll pigments may confer a greater capacity to respond rapidly to fluctuations in light environment (Lavaud et al. 2007), in part reflecting the slower rate of recycling of Dt to Dd compared to the de-epoxidation step. The proposed antioxidant function of DMSP involves irreversible, enzymatic cleavage to DMS, which may be oxidised to dimethyl sulphoxide or to methane sulphinic acid (Sunda et al. 2002). Continuous de novo synthesis of DMSP would be required in the light in order to maintain sufficient intracellular concentrations. This apparently irreversible antioxidant cascade contrasts with the recycling of xanthophyll pigments and may result in the need for greater adaptive variation in intracellular DMSP pools in response to differing exposure to photoinhibitory light levels. This may explain the ~40-fold variation in DMSP/chl *a* compared to an only ~10-fold variation in (Dd + Dt)/chl *a* observed during the annual cycle at L4 (Fig. 4) and the differences in levels of significance of their relationships to PAR dose (Fig. 7, Table 1).

MAAs protect cells from damage caused by UV irradiance by absorbing high-energy photons and dissipating the energy as heat. However, evidence from *in vitro* models that certain MAAs, in particular mycosporine glycine, act as antioxidants in addition to being sunscreens (reviewed in Oren & Gunde-Cimerman 2007) increases the relevance of the comparison between the accumulation of DMSP and MAAs in the present study. Like DMSP, the occurrence and intracellular concentrations of UV-absorbing compounds varies considerably between microalgal species and strains (Jeffrey et al. 1999). Hence, the seasonal variations observed in DMSPt and MAA concentrations and, in particular, in chlorophyll-specific concentrations of DMSPt and MAAs (Fig. 4) are likely to be driven primarily by taxonomic succession. However, this does not detract from the presumption that the physiological requirements of the phytoplankton to synthesise DMSP, xanthophyll pigments and MAAs are an adaptive response to the environment in which they occur and will be reflected in the seasonal variations in biomass-specific concentrations. Differences between taxa in the photoprotective strategies they employ may explain the variations in specific details between the patterns of DMSPt, Dd + Dt and MAAs observed particularly during summer months (Fig. 4). The dinoflagellate taxa that dominated DMSPt production during stratification of the water column may not have been the taxa that invested most resources in xanthophyll pigment synthesis or that contributed most to MAA production, hence the comparatively low levels of significance between peridinin and Dd + Dt and MAA (Table 1). Whilst many factors may govern taxonomic succession, energy investment in photoprotective and antioxidant mechanisms, including possibly intracellular DMSP accumulation, xanthophyll pigments and MAAs, may confer a competitive advantage under the stratified, high-light and high-UV environment during summer months in the western English Channel and may, thereby, contribute to the patterns of seasonal taxonomic succession.

The low nutrient concentrations that coincided with stability of the water column and high PAR dose may have contributed to the seasonal pattern in DMSPt concentrations observed at L4. The highly significant inverse relationship between nitrate concentration and log-transformed DMSP/chl *a* ratio (Fig. 8) indicates that a combination of nitrate limitation and irradiance determined levels of DMSP accumulation by phytoplankton. Several reasons why nitrogen limitation may increase DMSP intracellular accumulation have been proposed. Nutrient limitation of photosynthesis may elevate levels of oxidative stress, boosting the up-regulation of antioxidant systems, including possibly DMSP and its breakdown products (Sunda et al. 2007). Additionally, the capability to synthesise nitrogen-free osmolytes, such as DMSP, may be an advantage to phytoplankton faced with low nitrogen availability (Stefels 2000). However, low nitrate concentrations may not necessarily indicate nutrient limitation. Regenerated ammonium, dissolved organic nitrogen and nitrogen fixation may provide alternative sources of nitrogen during stratified periods in the summer in the western English Channel (Rees et al. 2009). It is possible that inconsistent availability of these alternative nitrogen sources played a part in the highly variable DMSP/chl *a* ratio observed at low nitrate concentrations at L4 (Fig. 8) and should be considered when interpreting the impact of nitrogen availability in natural phytoplankton communities. Alternatively, the high variability in DMSP/chl *a* at low nitrate concentrations at L4 may have been a result of taxonomic succession of the major DMSP-producing phytoplankton. In culture, different phytoplankton taxa have shown a wide range of responses in intracellular DMSP concentrations when grown under varied levels of nutrient availability (reviewed in Stefels et al. 2007).

In conclusion, the seasonal study in the western English Channel suggests that the classic 'DMS summer paradox' (Simó & Pedrós-Alió 1999) of particularly high concentrations of DMS relative to DMSP in shallow, mixed layer conditions typical of summer months may only partially exist in temperate shelf seas. This may be a consequence of the substantial part that taxonomic succession plays in determining DMSP concentrations, and possibly the proportion of DMS produced from DMSP, in these temperate waters. In particular, the 2 peaks in DMSPt during stratified conditions in the summer months were largely the product of 2 different dinoflagellate species, but were distinctly different in terms of the relative DMS to DMSPt concentrations. The chlorophyll-specific accumulation of DMSPt in phytoplankton is closely related to irradiance levels in the temperate shelf seas of the western English Channel. In combination with similar trends observed in the accumulation of xanthophyll pigments that act to prevent photoinhibition and reactive oxygen species production, and in relative concentrations of MAAs, which act as both UV-absorbing compounds and antioxidants, this lends indirect support to the photoprotective role of DMSP. The requirements for this role may be reinforced by low nitrate availability that occurred in parallel to elevated PAR dose and by increased UVB exposure during stratification of the water column. DMSP may function by decreasing the deleterious physiological effects of a combination of too much PAR, damaging UV radiation and nutrient limitation. However, direct physiological evidence of the nature of these roles is still lacking and warrants further study. This, in combination with more specific

identification of which components of the phytoplankton communities were responsible for DMSP and DMS production, would help explain when, why and how much DMSP and DMS synthesis occurs. Explicit inclusion of DMSP production processes and the controls on that production, including a photophysiological function, may ultimately improve the predictive skill of mechanistic models of DMS biogeochemistry, particularly in temperate waters.

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