

Fate of dimethylsulfoniopropionate (DMSP) during the decline of the northwest Atlantic Ocean spring diatom bloom

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ABSTRACT: A 7 d Lagrangian process study of the biogeochemical cycling of dimethylsulfoniopropionate (DMSP) and dimethylsulfide (DMS) was conducted within a decaying diatom bloom in the northwest Atlantic Ocean in spring 2003. Ambient profiles of DMSP and DMS were surveyed daily in the water column and were used to estimate *in situ* net transformation rates. Phytoplankton and bacterioplankton abundance were determined within the surface mixed layer (SML) as well as at the deep chlorophyll maximum (DCM), and sinking fluxes of particulate DMSP (DMSP_p) below 75 to 100 m were assessed using free-drifting particle interceptor traps. Chlorophyll *a* (chl *a*) concentration and diatom abundance declined in the SML over the course of the study period, and the phytoplankton chl *a* biomass progressively settled above the nitracline forming the DCM. The decline of the diatom bloom coincided with the settling of DMSP_p out of the SML and the formation of a DMSP-rich layer at the DCM. The low daily sinking loss rate of DMSP_p at 75 m (<2% d⁻¹) provided confirmation of the efficient retention of DMSP_p at the DCM. The decaying bloom gave rise to an initial release of dissolved DMSP (DMSP_d) in the upper water column, which was rapidly consumed by the growing bacterial community. The rapid loss of DMSP_d was accompanied by significant increases in net production of DMS in the SML and fluxes of DMS to the atmosphere. Despite this increase in DMS dynamics, overall *in situ* net production rates remained fairly low during the 7 d period (≤0.4 nmol DMS l⁻¹ d⁻¹), suggesting that demethylation by the developing bacterial community dominated DMSP_d-consuming processes.

KEY WORDS: DMSP distribution · DMS production · Diatom bloom · Lagrangian study · Sinking flux · Northwest Atlantic

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INTRODUCTION

Dimethylsulfide (DMS) is a trace gas involved in the transfer of sulfur from the ocean to the atmosphere through biogeochemical cycling (Simó 2001). Marine emissions of DMS have an important role as precursors of atmospheric sulfur-containing aerosols that influence the Earth's climate system through direct

backscatter of solar radiation and through cloud formation (Charlson et al. 1987). DMS is a product of the enzymatic cleavage of dimethylsulfoniopropionate (DMSP), an osmolyte produced by various groups of phytoplankton including dinoflagellates, prymnesiophytes and diatoms (Keller et al. 1989). Recent studies have demonstrated that DMSP and DMS contribute significantly to the fluxes of carbon, sulfur and energy

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through the marine microbial food web (Kiene et al. 2000, Simó 2001).

DMSP production is thought to vary with the phytoplankton physiological state, which depends on light availability (Matrai et al. 1995, Sunda et al. 2002), nutrient supply (Stefels & van Leeuwe 1998) and water temperature (Sheets & Rhodes 1996). The release of DMSP into the water column occurs when phytoplankton become senescent due to nutrient limitation (Nguyen et al. 1988), are intensively grazed by zooplankton (Dacey & Wakeham 1986, Levasseur et al. 1996), or undergo viral lysis (Hill et al. 1998). Moreover, DMSP in its particulate form (DMSP_p) may be lost from surface waters through incorporation into the food chain via its ingestion by grazers (Wolfe et al. 1994), and by sedimentation via zooplankton fecal pellets or aggregated senescent cells (Corn et al. 1994).

Once dissolved in seawater, DMSP is a labile compound that is readily consumed by heterotrophic bacteria, which transform dissolved DMSP (DMSP_d) not only into DMS, but predominantly into methanethiol (MeSH) via a demethylation/demethiolation pathway (Kiene et al. 2000). This metabolic pathway may lead to the incorporation of sulfur into cellular proteins, thus acting as a major control on DMS emissions to the atmosphere. Recent studies have also suggested that DMSP can be taken up by widespread cyanobacteria such as *Synechococcus* (Malmstrom et al. 2005) and *Prochlorococcus*, and even by eukaryotic phytoplankton such as diatoms (Vila-Costa et al. 2006). Bacterial consumption of DMS (Kiene & Bates 1990), along with its photolysis in surface waters (Kieber et al. 1996), constrains its flux to the atmosphere.

The North Atlantic Ocean in early spring is characterized by blooms of large diatoms and high chlorophyll *a* (chl *a*) concentrations. Although these seasonal events have been fairly well studied in terms of carbon cycling, especially during the Joint Global Ocean Flux Study (JGOFS) decade with projects such as the North Atlantic Bloom Experiment (NABE) (Ducklow & Harris 1993), many uncertainties surrounding sulfur cycling and the contribution of these diatom blooms to DMS production remain. Despite their low DMSP quotas, diatoms may significantly contribute to the release of DMSP and the production of DMS, particularly during the decline of spring blooms (Andreae et al. 1985, Matrai & Vernet 1997). It has also been proposed that the collapse of algal blooms and the concurrent release of DMSP_d may significantly enhance the capacity of bacterial communities to break down DMSP_d and DMS (Kiene & Service 1991, Levasseur et al. 1996). However, recent studies suggest that DMS production results from a more complex interplay between algal bloom dynamics and the influence it exerts on bacterial DMSP and DMS metabolism (Levasseur et al. 2006, Merzouk et al. 2006).

While previous studies of open-ocean blooms of diatoms in the North Atlantic have surveyed water column pools of DMSP and DMS and have estimated rates of DMS flux to the atmosphere (Andreae et al. 1985, 2003), very little information is available on their cycling rates (Scarratt et al. 2000b, Levasseur et al. 2004), especially during the decaying phase of these blooms. This study investigates the processes by which bloom development and the associated changes in the trophic web influence the distribution of DMSP and DMS, and quantifies the *in situ* net transformation rates of DMSP and DMS during the declining stage of a diatom bloom in the northwest Atlantic Ocean.

MATERIALS AND METHODS

Study area and Lagrangian framework. The 7 d Lagrangian study extended from 25 April to 1 May 2003 and was conducted aboard the CCGS 'Hudson' on the continental rise southeast of Nova Scotia, Canada (Station L; water depth 3500 m; Fig. 1). Prior to the cruise, ocean color data were obtained from the NASA Sea-viewing Wide Field-of-view Sensor (SeaWiFS), allowing the characterization of surface chl *a* distribution in the area. The movement of the water mass was monitored continuously by a drifting buoy equipped with an underwater drogue and an ARGOS transponder (Fig. 1, see Pommier et al. 2008 for details).

Field sampling. Vertical profiles of salinity, temperature and *in vivo* fluorescence were determined using a CTD probe (Sea-Bird SBE 9) and a fluorometer (WSD-818P) mounted on a rosette sampler. Seawater samples for the determination of chl *a*, DMSP and DMS concentrations were collected at 7 depths from 2 to 200 m with 10 l Scripps bottles. Water samples for DMSP and DMS net rate measurements as well as phytoplankton and bacterioplankton enumeration were collected at 10 m depth in the surface mixed layer (SML). For concentration and rate measurement, seawater was drawn from each bottle using C-flex[®] (Cole-Parmer) tubing. When obtaining the water samples, great care was taken to avoid introducing air bubbles into the samples. The water samples were pre-screened on a 202 µm Nitex mesh to remove large grazers.

Chl *a*, DMSP and DMS analyses. Concentrations of chl *a* were measured aboard the ship following the fluorometric method of Parsons et al. (1984) as described in Pommier et al. (2008). Samples for the determination of DMSP_p, DMSP_d, and DMS were prepared by gravity filtration of 71 ml of seawater through 47 mm Whatman GF/F filters (nominal pore size of 0.7 µm). DMS samples were prepared by carefully decanting 24 ml of filtrate into serum bottles, leaving no headspace. All

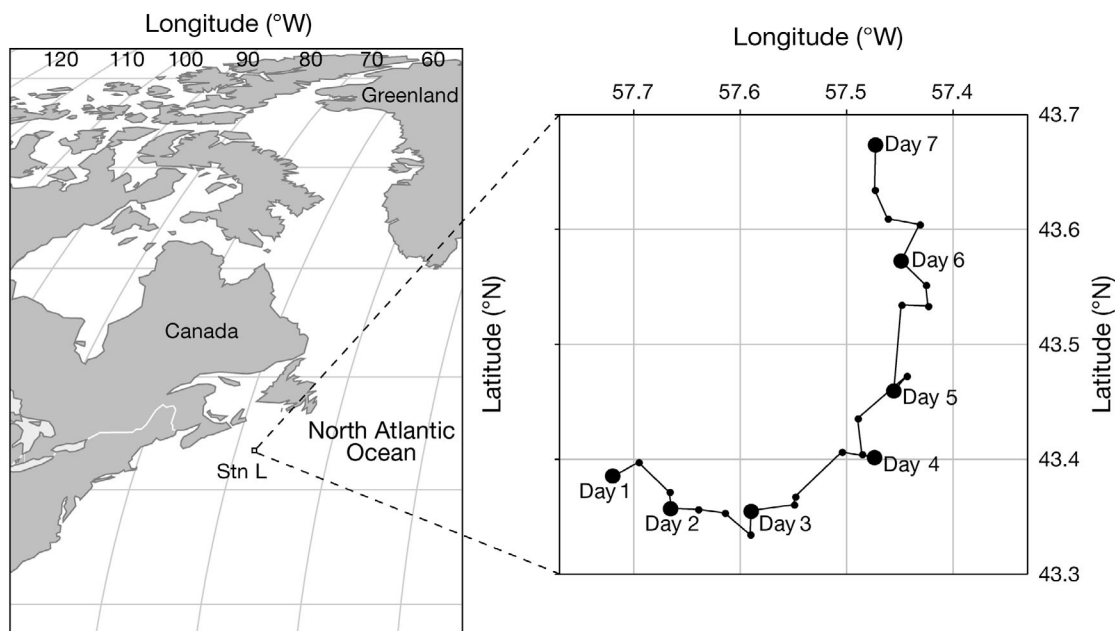


Fig. 1. Location of the Lagrangian station in the northwest Atlantic Ocean over the 7 day period (Day 1 to Day 7). Position of the drifting buoy at every 6 h time point is indicated

serum bottles were immediately sealed with butyl rubber septa and aluminum crimps. DMS samples were then analyzed on board the ship as quickly as possible, usually within a few minutes of collection. For $\text{DMSP}_d + \text{DMS}$ samples, 24 ml serum bottles containing 1 ml of KOH solution (10 M) were filled with 23 ml of filtrate and then sealed. Concentrations of DMSP_d were calculated by subtracting DMS from $\text{DMSP}_d + \text{DMS}$. DMSP_p samples were obtained by placing the filter in a serum vial containing 23 ml of deionized water and 1 ml of KOH solution (10 M). In view of recent evidence that the common filtration procedure, as carried out during this study, may result in artificial release of DMSP from phytoplankton cells (Kiene & Slezak 2006), DMSP_d concentrations measured in our study should be considered with caution. However, during this study, DMSP_d concentrations did not exceed 4 nmol l^{-1} during a period (bloom senescence) when large amounts of dissolved organic matter are thought to be released in the water column. The range of DMSP_d concentrations observed throughout the water column (0.2 to 3.9 nmol l^{-1}) is near the range of DMSP_d concentrations (0.4 to 2.8 nmol l^{-1}) that have been measured using a less disruptive filtration method (small volume gravity filtration) in a broad span of oceanic water types (Kiene & Slezak 2006). Thus, we concluded that DMSP_d values observed in the present study are real and result essentially from ecological processes.

Size fractionation of DMSP_p was conducted by gravity filtration of 280 ml of water through a sequential filtration apparatus (Sartorius) with 3 stages (pore

sizes of 20 and 5 μm (Magna Nylon filters) and 0.7 μm (Whatman GF/F filters). The filters were then placed in 24 ml serum bottles containing 23 ml of deionized water and 1 ml of KOH solution (10 M). All DMSP samples were kept in the dark at 4°C for at least 24 h and analyzed within a week of collection. Subsamples of DMSP and DMS were withdrawn from the 24 ml serum vials and sparged using a purge and trap system in line with a Varian 3400 or 3800 gas chromatograph (GC) equipped with a pulsed flame photometric detector (PFPD) (see Scarratt et al. 2000a for details). For the analysis of DMSP, the GC was calibrated with milliliter injections of a $5 \mu\text{g ml}^{-1}$ solution of hydrolyzed DMSP (Research Plus). DMS samples were calibrated against microliter injections of DMS, diluted with Ultra High Purity grade helium prepared using a permeation tube (Certified Calibration by Kin-Tek Laboratories) maintained at 40°C . The analytical precision for DMSP and DMS was better than 4%.

Phytoplankton and bacterioplankton enumeration.

Phytoplankton identification and enumeration were performed on samples preserved in acidic Lugol's solution and buffered formaldehyde using a settling column and inverted microscope (Utermöhl 1931). Samples for the determination of bacterioplankton abundance were preserved with glutaraldehyde (1% final concentration) and kept in sterile 5 ml polystyrene Falcon tubes in the dark at -75°C . For the enumeration of bacteria, samples were stained with SYBR Green-I and analyzed by flow cytometric analysis (Becton

Dickinson, FACS Calibur analyser) following the methods of Brussaard et al. (2000) and references therein.

DMSP_p sinking fluxes. The sinking fluxes of DMSP_p were measured using free-drifting particle interceptor traps deployed for 24 h on 26 April (Day 2), 28 April (Day 4) and 30 April (Day 6). Detailed information on trap specifications, handling and deployment is available in Pommier et al. (2008). Briefly, the cylindrical PVC traps, which had an aspect ratio (height : diameter) of 7, were deployed at 50, 75, 100, 125 and 150 m. Only the results from the traps deployed at 75 or 100 m have been considered in this study. Before deployment, the traps were filled with deep (ca. 1000 m) seawater, pre-filtered through 0.22 µm Millipore membrane filters, and supplementary salt was added to create a dense layer within the traps. No preservatives were added to the traps, which were installed in pairs at each depth on the mooring line. Upon recovery, the traps were allowed to settle in a dark cool room for 8 h. After that sedimentation period, the supernatant was carefully removed and DMSP_p concentrations were measured from the residual volume of the trap (900 to 1000 ml). The daily sinking fluxes of DMSP_p (in µmol m⁻² d⁻¹) were calculated as follows:

$$\text{Sinking flux} = (C_{\text{trap}} \times V_{\text{trap}}) / (A_{\text{trap}} \times T) \quad (1)$$

where C_{trap} is the concentration of DMSP (µmol l⁻¹), V_{trap} is the bottom volume of the trap after sedimentation (l), A_{trap} is the surface area of the trap (m²), and T is the duration (d) of trap deployment.

The daily sinking loss rate of suspended DMSP_p (in % d⁻¹) in the upper 75 m of the water column due to sinking export was estimated using the following equation:

$$\text{Daily loss rate} = (\text{sinking flux} / C_{\text{int}}) \times 100 \quad (2)$$

where DMSP_p sinking flux at 75 or 100 m is computed from Eq. (1) and C_{int} is the integrated DMSP_p concentration in the upper 75 m of the water column.

DMS(P) net production rates. *In situ* net production rates of DMSP_p, DMSP_d and DMS (in µmol m⁻² d⁻¹) were estimated from changes in the integrated concentrations of each sulfur compound between 2 consecutive sampling days according to:

$$\text{Net production rate} = (C_{\text{int}(t+1)} - C_{\text{int}(t)}) / T \quad (3)$$

where $C_{\text{int}(t+1)}$ and $C_{\text{int}(t)}$ are depth-integrated concentrations on Day $t+1$ and Day t , respectively, and T is the time interval (i.e. 1 d). Rates were computed for 2 strata: (1) from surface to 10 m and (2) from 10 m to the depth of the DCM. Net production rates (nmol l⁻¹ d⁻¹) were also computed for discrete depths (i.e. 10 m and depth of the DCM).

The fraction of the net *in situ* production of DMSP_p recovered in the traps during their deployment (in %) was calculated according to:

$$\text{Recovered fraction} = \frac{\text{sinking flux}}{\text{net production rate}} \times 100 \quad (4)$$

where DMSP_p sinking flux at 75 or 100 m is computed from Eq. (1) and DMSP_p net production rate, integrated from surface to 75 m, is computed from Eq. (3).

Ventilation of DMS. The sea-to-air flux of DMS was calculated on each sampling day from the product of the sea surface DMS concentration (at ca. 5 m) and a DMS air–sea exchange coefficient, following the Nightingale et al. (2000) parameterization. Wind speed was recorded every 4 h with the ship's on-board system.

Statistical analyses. Kendall's rank correlation coefficient (τ) was used to seek the relationship between 2 variables, while Wilcoxon's signed ranks test was used to compare paired variates (Sokal & Rohlf 1981).

RESULTS

Lagrangian setting and water column structure

The water mass chosen for the Lagrangian study was successfully tracked and sampled for 7 d as confirmed using Temperature–Salinity (T–S) diagrams (Pommier 2007). Surface water characteristics remained fairly stable throughout the study period as shown by the prevailing physical and chemical conditions in Table 1. Salinity at 10 m ranged from 32.63 to 32.72. Temperature at 10 m gradually increased from 2.6 to 3.4°C. A deepening of the SML to 18–26 m occurred from Days 4 to 7, coinciding with episodes of stronger wind speeds during the nights of Days 3 to 4 (average 16 m s⁻¹) and Days 5 to 6 (average 11 m s⁻¹). Nitrate concentrations at 10 m depth were 0.9 µmol l⁻¹ during the first 2 d and rapidly decreased near the limit of detection for the rest of the sampling period. Chl *a* concentration in the SML was initially 6.1 µg l⁻¹ and decreased progressively to reach 1.1 µg l⁻¹ by the end of the study.

A noticeable feature of the study area was the formation of a deep chlorophyll maximum (DCM) located at the base of the euphotic zone just above the nitracline (ca. 45 m) as reported in Pommier (2007). The depth of the DCM remained fairly constant throughout the study period (40 to 50 m) and chl *a* concentrations ranged from 8.1 to 16.1 µg l⁻¹. Salinity and temperature remained stable in the DCM from Days 1 to 7 with values varying between 32.91 and 33.00, and between 1.7 and 2.2°C, respectively. Nitrate concentrations at the DCM were higher than those from the SML, varying between 0.3 and 4.3 µmol l⁻¹.

Table 1. Physical, chemical and biological characteristics of seawater sampled at a fixed depth of 10 m in the surface mixed layer (SML) and at the depth of the deep chlorophyll maximum (DCM) in spring 2003. SML depth and nitrate concentrations from Pommier et al. (2007)

Date	Day	SML or DCM (m)	Sampling depth (m)	Salinity	Temperature (°C)	Nitrate ($\mu\text{mol l}^{-1}$)	Chl <i>a</i> ($\mu\text{g l}^{-1}$)
SML							
25 Apr	1	10	10	32.63	2.6	0.9	6.1
26 Apr	2	12	10	32.69	2.8	0.9	4.8
27 Apr	3	11	10	32.69	3.1	<0.05	2.9
28 Apr	4	23	10	32.72	3.1	<0.05	3.5
29 Apr	5	19	10	32.64	3.1	<0.05	2.2
30 Apr	6	26	10	32.69	3.3	<0.05	1.5
01 May	7	18	10	32.67	3.4	<0.05	1.1
DCM							
25 Apr	1	45	45	33.00	2.0	2.4	14.6
26 Apr	2	43	43	32.91	2.0	3.5	11.1
27 Apr	3	45	45	32.91	2.2	0.3	16.1
28 Apr	4	50	50	32.93	1.9	2.9	16.1
29 Apr	5	50	50	32.92	1.9	0.9	10.4
30 Apr	6	50	50	32.98	2.1	2.7	8.1
01 May	7	45	45	32.92	1.7	4.3	11.5

Plankton community composition and abundance

Total phytoplankton abundance displayed a significant decrease ($t = -0.62$, $p < 0.05$) over the course of the Lagrangian study at 10 m from 0.91×10^6 cells l^{-1} on Day 1 to 0.43×10^6 cells l^{-1} on Day 7 (Fig. 2A). On Days 1 and 2, the phytoplankton community was largely represented by centric diatoms (Fig. 2C) of the genera *Chaetoceros* spp. (49 to 55% of total diatoms), and *Thalassiosira* spp. (14 to 24% of total diatoms). Furthermore, an 85% reduction of total diatom abundance was observed from Days 1 to 7 in the SML. The second most abundant group was unidentified phytoplankton (mostly flagellates), constituting from 28 to 53% of total

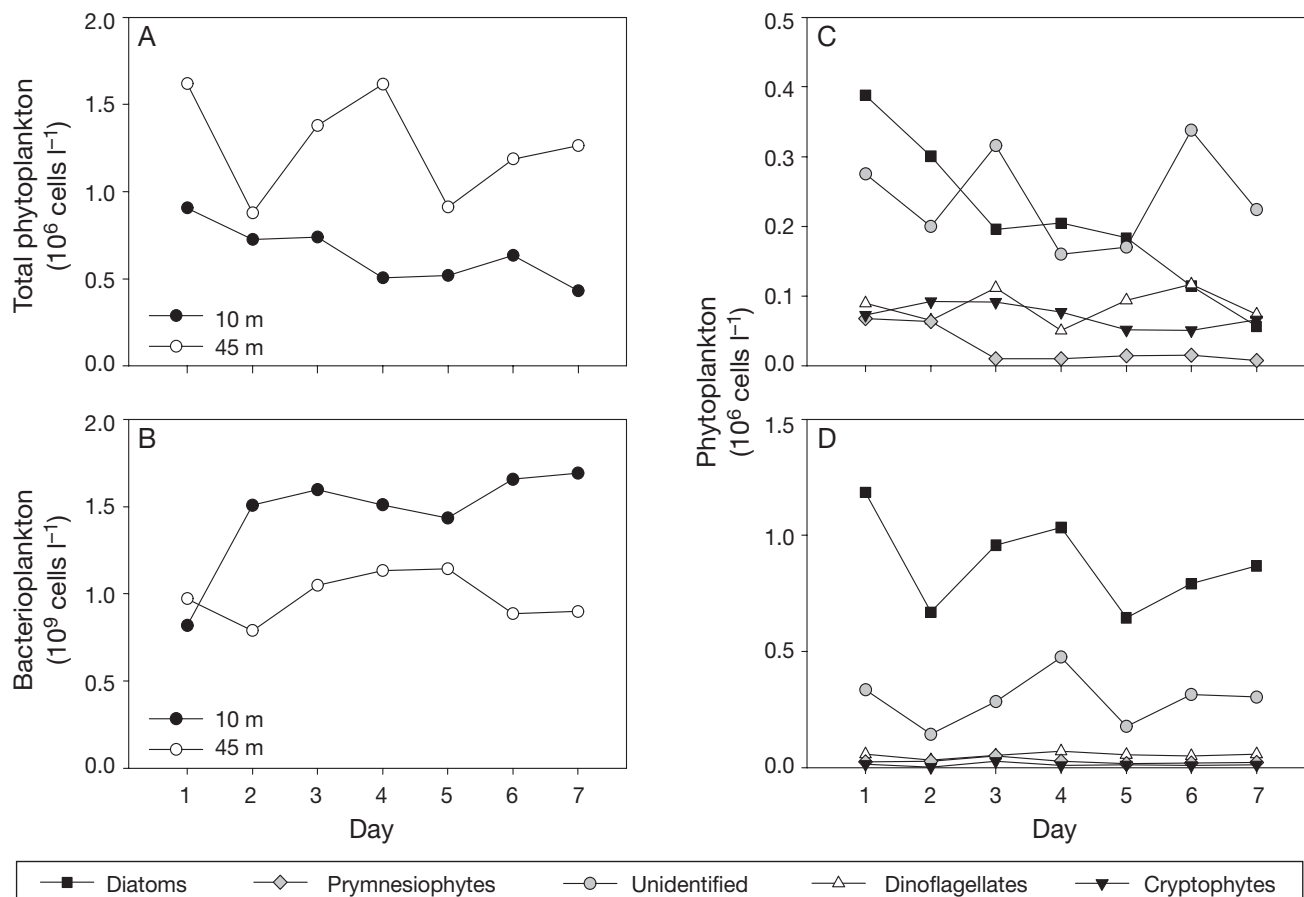


Fig. 2. Time series of (A) total phytoplankton abundance in the surface mixed layer (SML, 10 m) and at the deep chlorophyll maximum (DCM, 43 to 50 m), (B) bacterioplankton abundance in the SML and at the DCM, and phytoplankton community composition (C) in the SML and (D) at the DCM throughout the Lagrangian study period

phytoplankton abundance. By Day 6, a net shift in dominance occurred, and small unidentified nanoflagellates (2 to 5 μm) prevailed numerically over the rest of the community. The abundance of other phytoplankton groups such as dinoflagellates, cryptophytes and prymnesiophytes remained fairly stable. While the diatom population was declining in the SML, bacterial abundance increased almost 2-fold between Days 1 and 2, with values rising from 0.82×10^9 cells l^{-1} to 1.51×10^9 cells l^{-1} , and further increased to 1.69×10^9 cells l^{-1} by Day 7 of the study period (Fig. 2B)

The DCM was characterized by consistently higher total phytoplankton abundance than in the SML (Wilcoxon signed rank test, $p < 0.05$), with concentrations ranging from 0.9×10^6 cells l^{-1} to 1.6×10^6 cells l^{-1} (Fig. 2A). Diatoms contributed $70 \pm 4\%$ (mean \pm SD) of total phytoplankton abundance in the DCM during the 7 d period, while unidentified phytoplankton were the second most abundant group, representing $22 \pm 5\%$ of total phytoplankton abundance (Fig. 2D). As in the SML, a similar pattern of fairly stable and low abundance was observed for other phytoplankton groups at the DCM. Bacterioplankton abundance at the DCM was lower than in the SML (Wilcoxon signed rank test,

$p < 0.05$) and remained stable between 0.79 and 1.14×10^9 cells l^{-1} (Fig. 2B).

Vertical distribution of chl *a* and sulfur compounds

Chl *a* showed high vertical variability throughout the sampling period with highest concentrations forming the DCM (up to $16 \mu\text{g l}^{-1}$, Fig. 3A) found above the nitracline (ca. 50 m). As the phytoplankton bloom aged, chl *a* concentrations at 10 m decreased ($\tau = -0.91$, $p < 0.05$) from $6.1 \mu\text{g l}^{-1}$ to $1.1 \mu\text{g l}^{-1}$. Below the DCM, concentrations of chl *a* decreased with increasing depth.

On Day 1, concentrations of DMSP_p (Fig. 3B) were distributed more evenly within the surface and subsurface waters. In the SML (10 m), concentrations of DMSP_p peaked on Day 2, reaching a maximum of 29.3 nmol l^{-1} , which was followed by a significant decrease to 12.4 nmol l^{-1} ($\tau = -0.62$, $p < 0.05$) by Day 7. As the study progressed, the highest concentrations of DMSP_p (maximum of 47 nmol l^{-1} on Day 6) were found in a narrow band that developed and remained near the DCM (ca. 45 m). Below the subsurface maximum, con-

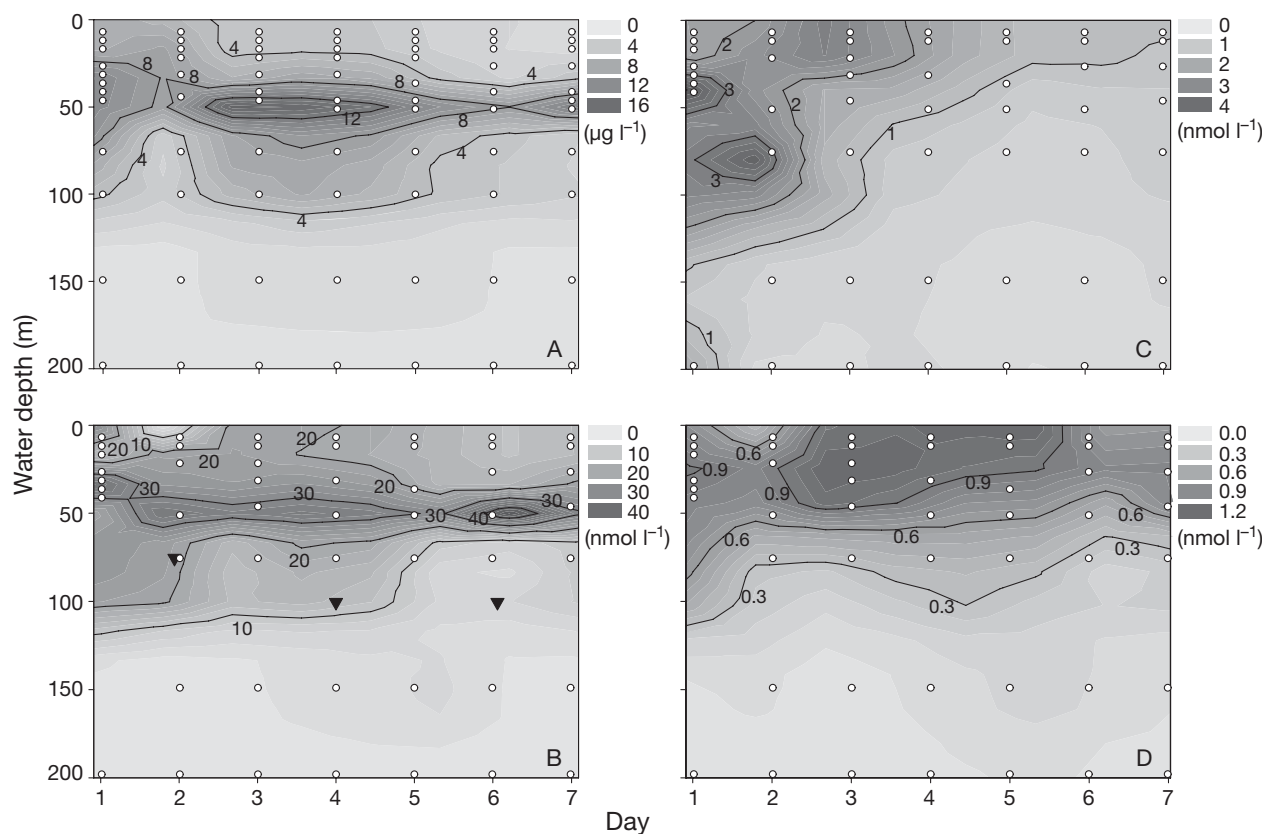


Fig. 3. Contour plots for (A) chl *a* ($\mu\text{g l}^{-1}$), and (B) particulate dimethylsulfoniopropionate (DMSP_p), (C) dissolved DMSP (DMSP_d) and (D) dimethylsulfide (DMS) (nmol l^{-1}) during the Lagrangian study. This figure was produced with the SigmaPlot software, using the inverse-distance smoothing. O: sampling depths, ▼: depths of the free-drifting particle interceptor traps (B only)

centrations of DMSP_p tended to decline towards the bottom of the water column.

Vertical profiles of DMSP_d (Fig. 3C) exhibited a different pattern than the one observed for DMSP_p . Maximum concentrations of DMSP_d (ca. 4 nmol l^{-1}) occurred at 40 m depth on Day 1 and 75 m depth on Day 2. These higher localized concentrations of DMSP_d were followed by a rapid depletion of DMSP_d stocks throughout the different layers of the water column, which represented an overall 80% decrease. At 10 m, DMSP_d peaked on Day 2 (3.9 nmol l^{-1}), followed by a significant decrease to 0.7 nmol l^{-1} ($\tau = -0.71$, $p < 0.05$) by the last day of the study. By Day 5, DMSP_d was rather uniformly distributed from surface waters down to 200 m, with values below 1.5 nmol l^{-1} .

Unlike DMSP_d , DMS stocks showed a fairly constant vertical structure during the entire sampling period (Fig. 3D). Concentrations of DMS were relatively homogeneous in the first 45 m of the water column, and maximum values (1.0 to 1.1 nmol l^{-1}) occurred in the SML on Days 3 through 5. DMS profiles exhibited a steady decrease below the DCM down to 200 m.

Size fractionation of DMSP_p

Much of the DMSP_p in the SML (65 to 80%) was associated with the microplankton fraction ($>20 \mu\text{m}$), a size range dominated by diatoms (Fig. 4A). While the bloom receded, the contribution of the $>20 \mu\text{m}$ fraction to the total DMSP_p pool decreased. The 5 to 20 μm and 0.7 to 5 μm size fractions accounted for a smaller proportion of the total DMSP_p pool, being 17 to 29% and $<7\%$, respectively. While the DCM microplankton fraction ($>20 \mu\text{m}$) displayed more day-to-day variations, its contribution to the total DMSP_p concentration (67 to 86%) remained comparable with the one found in the SML. The share of the total DMSP_p to the 5 to 20 μm and 0.7 to 5 μm fractions were 12 to 30% and 2 to 6%, respectively.

Transformation rates and fluxes of DMSP and DMS

Within the first 10 m of the water column (0 to 10 m), net changes of integrated concentrations of DMSP_p were characterized by *in situ* net production rates varying between 0.4 and $12.5 \mu\text{mol m}^{-2} \text{ d}^{-1}$, except on Day 5, when a net loss occurred ($-28.3 \mu\text{mol m}^{-2} \text{ d}^{-1}$, Fig. 5A). DMSP_p *in situ* net production/loss rates between 10 m and the DCM (ca. 45 m) were characterized by transient peaks of net production and net loss, with rates fluctuating between 262.4 and $-360.0 \mu\text{mol m}^{-2} \text{ d}^{-1}$ (Fig. 5D). During the study period, the fluctuations in standings stocks translated into mean net

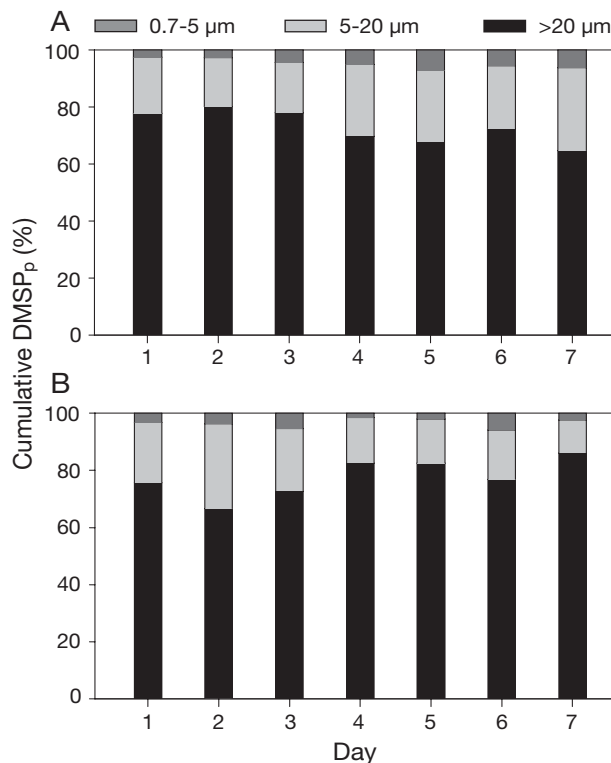


Fig. 4. Time series of the relative cumulative concentrations of DMSP_p (%) into 3 size fractions (0.7 to $5 \mu\text{m}$, 5 to $20 \mu\text{m}$ and $>20 \mu\text{m}$) in (A) the surface mixed layer (SML, 10 m) and (B) at the deep chlorophyll maximum (DCM, 43 to 50 m) throughout the Lagrangian study

losses of DMSP_p both at the 0 to 10 m and 10 m to DCM intervals (-1.41 and $-4.59 \mu\text{mol m}^{-2} \text{ d}^{-1}$, respectively).

In situ net production rates of integrated DMSP_d (Fig. 5B,E) exhibited a similar trend throughout the first 50 m of the water column. The first day of the study was characterized by net production rates of $8.7 \mu\text{mol m}^{-2} \text{ d}^{-1}$ (0 to 10 m) and $24.0 \mu\text{mol m}^{-2} \text{ d}^{-1}$ (10 m to DCM). On the following days, an overall net loss of DMSP_d within the first 45 m of the water column was reflected by negative rates ranging from -1.0 to $-15.6 \mu\text{mol m}^{-2} \text{ d}^{-1}$, except on Day 5, when the *in situ* net production rate between 0 and 10 m was $1.2 \mu\text{mol m}^{-2} \text{ d}^{-1}$. Variations in pools of DMSP_d resulted in mean net losses throughout the top 45 m of the water column (-0.21 and $-4.43 \mu\text{mol m}^{-2} \text{ d}^{-1}$ between 0 and 10 m and 10 m and DCM, respectively).

Net changes in integrated concentrations of DMS within the first 10 m of the water column showed a trend of increasing net production from Day 1 until Day 5 ($\tau = 0.80$, $p < 0.05$), with rates ranging from 0.4 to $3.2 \mu\text{mol m}^{-2} \text{ d}^{-1}$ (Fig. 5C). On Day 6, a negative production rate of $-0.2 \mu\text{mol m}^{-2} \text{ d}^{-1}$ occurred. Between 10 m water depth and the DCM, changes in DMS concentrations during the first 2 d were characterized by net production rates of 4.2 and $8.2 \mu\text{mol m}^{-2} \text{ d}^{-1}$, respectively,

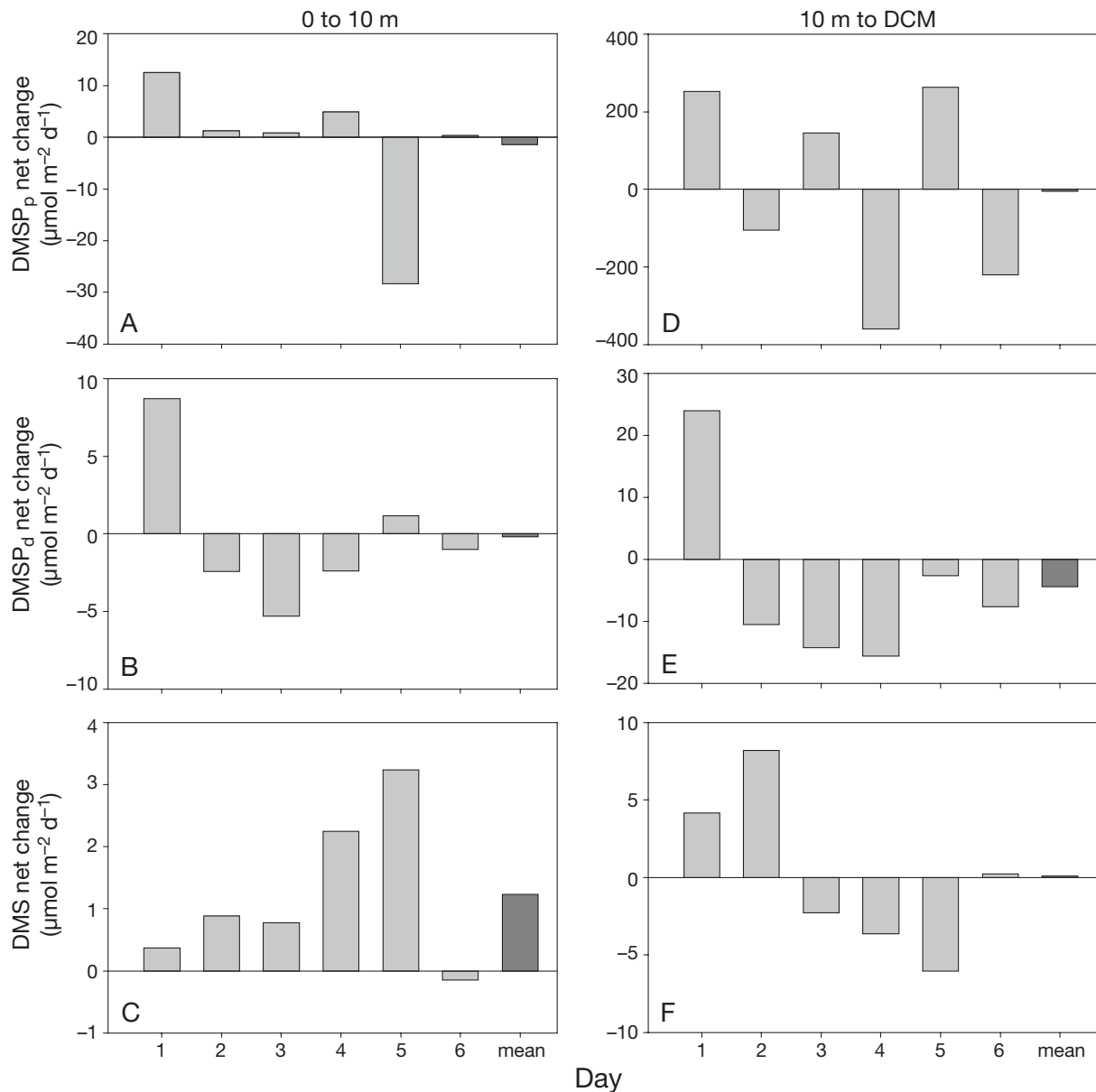


Fig. 5. Daily and mean net changes in vertically integrated stocks over the (A–C) 0 to 10 m and (D–F) 10 m to DCM depth intervals for (A,D) DMSP_p, (B,E) DMSP_d and (C,F) DMS throughout the Lagrangian study

which were followed by negative or weak net production ranging from -6.1 to $0.2 \mu\text{mol m}^{-2} \text{d}^{-1}$ (Fig. 5F). Fluctuations in standing stocks of DMS lead to a mean daily net production of 1.23 and $0.10 \mu\text{mol m}^{-2} \text{d}^{-1}$ at the 0 to 10 m and 10 m to DCM intervals, respectively.

The sinking fluxes of DMSP_p measured at 75 or 100 m were $28.5 \mu\text{mol m}^{-2} \text{d}^{-1}$ on Day 2, $27.1 \mu\text{mol m}^{-2} \text{d}^{-1}$ on Day 4, and decreased to $16.4 \mu\text{mol m}^{-2} \text{d}^{-1}$ on Day 6 (Table 2). The DMSP_p standing stock above the traps during these days ranged from 1792 to 2540 $\mu\text{mol m}^{-2}$, and the daily sinking loss rate of suspended DMSP_p at 75 to 100 m varied between 0.9 and 1.6% d^{-1} . *In*

situ net production rates of DMSP_p above the traps (0 to 75 m) displayed net losses ranging between -158.2 and $-583.5 \mu\text{mol m}^{-2} \text{d}^{-1}$. The fraction of the *in situ* net production of DMSP_p recovered in the traps during their deployment varied from 5% to 18% (Table 2).

Loss of DMS by ventilation to the atmosphere is shown in Fig. 6. Sea-to-air fluxes of DMS increased from $0.38 \mu\text{mol m}^{-2} \text{d}^{-1}$ on Day 1 to $3.05 \mu\text{mol m}^{-2} \text{d}^{-1}$ on Day 5, then decreased to below $0.70 \mu\text{mol m}^{-2} \text{d}^{-1}$ over the 2 following days, essentially following the changes in *in situ* net production of DMS and sea surface concentrations of DMS.

Table 2. Concentration, *in situ* net production rate and sinking flux of particulate DMSP (DMSP_p), daily sinking loss rate of suspended DMSP_p, and fraction of the *in situ* net production of DMSP_p recovered in traps during the deployment of the free-drifting particle interceptor traps on Days 2, 4 and 6. Concentrations and production rates are integrated from 0 to 75 m

Date	Day	Depth of trap (m)	Concentration ($\mu\text{mol m}^{-2}$)	Net production ($\mu\text{mol m}^{-2} \text{d}^{-1}$)	Sinking flux ($\mu\text{mol m}^{-2} \text{d}^{-1}$)	Loss rate (% d^{-1})	Recovered fraction (%)
26 Apr	2	75	1828	-158.2	28.5	1.6	18.0
28 Apr	4	100	2540	-583.5	27.1	1.1	4.6
30 Apr	6	100	1792	-206.7	16.4	0.9	7.9

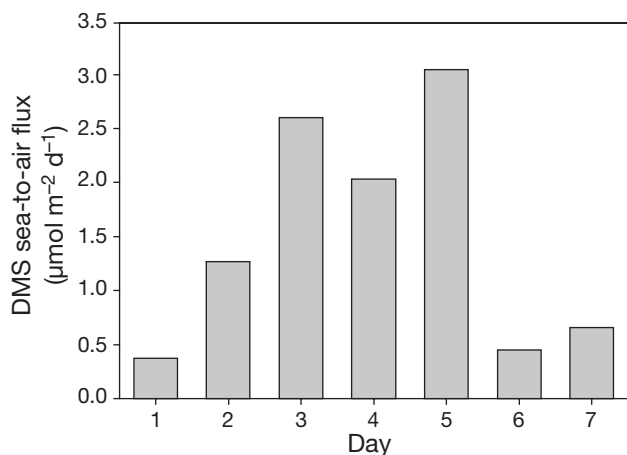


Fig. 6. Time series of DMS sea-to-air flux throughout the study

DISCUSSION

Bloom decline and plankton community change

The phytoplankton spring bloom was already in an advanced stage of development at the beginning of the cruise, as indicated by SeaWiFS satellite imagery showing decreasing chl *a* concentrations in surface waters (Forget et al. 2007). The initially high level of chl *a* ($6.1 \mu\text{g l}^{-1}$) and low level of nitrate ($<1 \mu\text{mol l}^{-1}$) measured in the SML (Table 1) were followed by a decrease in both chl *a* and nitrate concentrations, indicative of late-bloom conditions. Furthermore, a decline in total phytoplankton and diatom abundance in the SML (Fig. 2A,C) was observed, suggesting that the growth of primary producers was limited by the availability of nitrogen, a common finding during late spring and summer at temperate latitudes of the North Atlantic Ocean (Parsons & Lalli 1988, Platt et al. 1992, Pommier 2007). In the temperate North Atlantic, spring blooms often terminate with the sinking-out of large cells (such as diatoms) forming a major flux of particulate organic matter on their way down through the water column (Parsons & Lalli 1988, Honjo & Mangani 1993). However, the presence of the DCM at ca. 45 m (Fig. 3A) suggests that part of the settling phyto-

plankton accumulated near the nitracline during our study. The processes involved in the formation and maintenance of this DCM near the base of the euphotic zone are discussed by Pommier (2007).

The sedimentation of the senescent diatom population coincided with a shift in phytoplankton community dominance in the SML towards the middle of the survey period. Thereafter, small unidentified phytoplankton (predominantly flagellates 2 to 5 μm in size) prevailed in terms of abundance over the rest of the phytoplankton assemblage (Fig. 2C). Despite daily changes in abundance, diatoms remained dominant ($70 \pm 4\%$ of total phytoplankton abundance) during the entire study period at the DCM (Fig. 2D). Chl *a* concentration showed a strong positive correlation with diatom abundance both in the SML and at the DCM ($\tau = 0.91$, $p < 0.01$), but not to any other phytoplankton taxonomic groups, suggesting that diatoms were the principal contributors to phytoplankton biomass in the upper 45 m of the water mass.

During the decline of the diatom bloom, bacterial abundance doubled in the SML (Fig. 2B), suggesting that heterotrophic bacterial growth was favored by a release of dissolved organic matter from the senescent diatom cells. This assumption is reinforced by the increase in the percentage of total primary production released as extracellular carbon (percent extracellular release, PER) reported by Pommier (2007) throughout the decline of the bloom (from 10% to 30% between Days 1 and 6). As commonly observed in other marine systems, senescent algae provide an important amount of organic material, allowing the rapid development and maintenance of an active bacterial community (Cole et al. 1988). Bacterial abundance in the upper ca. 45 m of the water column varied between 0.8 and 1.7×10^9 cells l^{-1} , which is within the range normally observed in oceanic surface waters in spring (Ducklow 2000) and particularly during spring blooms in the North Atlantic Ocean (0.2 to 2.0×10^9 cells l^{-1}) (Ducklow et al. 1993). Bacterial stocks are known to be constrained by resource limitation and various removal processes such as bacterivory and lysis (Azam et al. 1983). However, in this study, it is more likely that the senescence of the spring bloom resulted in an abun-

dant organic pool, allowing the growth of the bacterial population, as evidenced by the increase in bacterial production (A. Merzouk unpubl. data).

Distribution of DMSP_p as a function of diatom sedimentation

During the study period, DMSP_p was redistributed within the upper ca. 45 m of the water column in association with the senescent phytoplankton population. While the decline of the diatom bloom progressed in the SML (Fig. 2C) and cells accumulated at the nitracline, concentrations of DMSP_p correspondingly decreased in surface waters and increased near the DCM (Fig. 3B). Over the 7 d period, the net loss of DMSP_p in the SML was reflected in the overall negative rates of change between 0 and 10 m (mean loss of 1.4 $\mu\text{mol m}^{-2} \text{d}^{-1}$, Fig. 5A) and at the discrete depth of 10 m (mean loss of 0.6 $\text{nmol l}^{-1} \text{d}^{-1}$, Table 3). The decrease of DMSP_p concentrations in surface waters appears to be mostly the result of the sedimentation of DMSP_p-containing phytoplankton out of the SML. Pathways of DMSP_p loss, such as heterotrophic grazing and excretion, viral lysis and other solubilization processes (Dacey & Wakeham 1986, Hill et al. 1998), may also have contributed to the reduction of DMSP_p in the SML. Evidence of these pathways, specifically during the first 2 d of the study, is reflected in the increase of DMSP_d concentrations (see section on rapid remineralization of DMSP_d), although no direct quantification of these solubilization processes is available. Storage of DMSP_p by microzooplankton is unlikely as a net loss of DMSP_p was measured in the >20 μm size fraction at 10 m (Fig. 4A).

The sedimentation of DMSP_p from the SML and its accumulation at the DCM allowed the formation of a distinct DMSP_p maximum. Changes in DMSP_p at the

DCM oscillated between net production and loss, with production dominating (mean gain of 2.4 $\text{nmol l}^{-1} \text{d}^{-1}$, Table 3). This led to the development of the DMSP_p maximum, located in a very narrow band around 45 m, which became increasingly pronounced during subsequent sampling days. The net production in DMSP_p found at the discrete depth of 45 m was not accompanied by a net production of DMSP_p between 10 m and the DCM (mean loss of 4.6 $\mu\text{mol m}^{-2} \text{d}^{-1}$, Fig. 5D), which confirms that the accumulation of DMSP_p was restricted to a narrow layer associated with the DCM. The net production of DMSP_p at the DCM could also be partly explained by a localized increase in primary production, as Pommier (2007) reported substantial production rates principally taking place among large phytoplankton cells ($\geq 5 \mu\text{m}$) near the DCM during the first 2 d of the study. However, Pommier (2007) concluded that, during the period investigated, phytoplankton growth at 45 m had limited influence on the maintenance of the DCM. Instead, sinking of phytoplankton from the nutrient-depleted SML was invoked as the main mechanism in the development of the DCM.

The range of DMSP_p concentrations observed at 10 m water depth in the present study (from 12 to 29 nmol l^{-1}) is lower than the global average particulate DMSP concentration presented in the Kettle et al. (1999) database. It is, however, consistent with a range of values reported for springtime conditions in the temperate North Atlantic Ocean. Scarratt et al. (2000b) reported DMSP_p concentrations of 9 and 39 nmol l^{-1} , respectively, for 2 distinct sites within the Northwest Continental Shelf (NWCS) biogeographic province, while Andreae et al. (2003) showed that values of DMSP_p near the surface of the water column were typically around 20 nmol l^{-1} in the Northeast Atlantic during springtime. As suggested in studies of the same region during spring (Scarratt et al. 2000b, Scarratt et al. 2002), the generally lower DMSP concentrations observed in this study illustrate the importance of improving estimates of the global database on regional and seasonal scales.

Diatoms were probably the principal source of DMSP_p during our study. Fractionation experiments in the SML showed that DMSP_p was recovered mainly in the >20 μm size fraction (Fig. 4A). Given that a significant positive relationship was found between diatom abundance and DMSP_p in the >20 μm size fraction ($\tau = 0.52$, $p < 0.05$), and that this size fraction accounted for a mean 73% of the total DMSP_p, it suggests that diatoms were responsible for most of the particulate pool of DMSP. Our results reinforce the idea that, although diatoms may not be rich in terms of cellular DMSP_p content, they may dominate the biogeochemical cycling of DMSP during large blooms (Andreae et

Table 3. Daily and mean *in situ* net changes in concentrations of DMSP_p and DMS ($\text{nmol l}^{-1} \text{d}^{-1}$) at a fixed depth of 10 m in the surface mixed layer (SML) and at the depth of the deep chlorophyll maximum (DCM, 43 to 50 m) in spring 2003

Date	Day	10 m		DCM	
		DMSP _p	DMS	DMSP _p	DMS
		(nmol l ⁻¹ d ⁻¹)		(nmol l ⁻¹ d ⁻¹)	
25 Apr	1	13.25	0.18	19.40	-0.01
26 Apr	2	-7.18	0.05	-2.23	0.30
27 Apr	3	-6.90	0.06	4.41	-0.42
28 Apr	4	0.21	-0.05	-7.91	0.10
29 Apr	5	-4.53	-0.36	16.16	-0.31
30 May	6	1.52	0.07	-15.33	0.35
Mean		-0.61	-0.01	2.42	0.00

al. 2003, Jiao et al. 2003). Furthermore, these results suggest that nutrient-limited diatom cells controlled the distribution of DMSP_p in the upper 45 m of the water mass during the decline of the northwest Atlantic spring bloom. The fate of the diatom population retained at the DCM is critical, since their massive export to depth would imply a potential for considerable loss of DMSP_p.

Even though an accumulation of DMSP_p took place near the nitracline, DMSP_p sinking fluxes were high below the nitracline (75 to 100 m) when compared with estimates from other, oceanic environments (Bates et al. 1994, Corn et al. 1994, Hatton 2002). Results obtained from the deployment of particle collectors on 3 different occasions show that the daily downward flux of DMSP_p varied between 16.4 and 28.5 $\mu\text{mol m}^{-2} \text{d}^{-1}$ (Table 2). The importance of sedimentation as a sink for particulate DMSP is still poorly understood and estimates vary widely in the literature (0.002 to 19.58 $\mu\text{mol m}^{-2} \text{d}^{-1}$, see review in Belviso et al. 2006). Results from our study show that the mean daily flux of DMSP_p at 75 to 100 m ($24.0 \pm 6.6 \mu\text{mol m}^{-2} \text{d}^{-1}$) is among the highest reported and is similar to the fluxes of DMSP_p measured during a mid-summer coccolithophore bloom in the northern North Sea (DMSP_p fluxes at 40 m ranging between 8.4 and 19.6 $\mu\text{mol m}^{-2} \text{d}^{-1}$, Hatton 2002). In our study, diatoms dominated the phytoplankton carbon sinking fluxes (51 to 97%) both below the DCM and at 150 m (Pommier et al. 2008), which highlights the important role of diatoms in controlling the distribution and sinking fluxes of DMSP_p from the upper layers of the water column during the decline of the northwest Atlantic spring bloom.

Despite these high sinking fluxes, sedimentation represented a minor removal pathway for DMSP_p during this study. Our results reveal that less than 2% (0.9 to 1.6%) of the suspended stock of DMSP_p in the upper 75 m was lost daily through sinking (Table 2), which is in accordance with daily loss rates of particulate organic carbon (POC) (varying between 1.3 and 2.0% in the upper 75 m of the water column) during the decline of the spring diatom bloom (J. Pommier pers. comm.). Similarly, Corn et al. (1994) and Hatton (2002) reported that sedimentation of DMSP had a minor effect on the upper-ocean budget of DMSP_p, with less than 1% of the standing stock being lost due to the sinking of this compound. However, loss rates reported in our study are lower than estimates from Kwint et al. (1996), who suggested that sinking zooplankton fecal pellets may represent up to 10% of the daily loss of DMSP production from surface waters. During a 48 h incubation experiment, Hatton (2002) demonstrated that 30 to 47% of the DMSP in the particle interceptor traps may be lost due to chemical and physical transformation processes such as microbial degradation and

conversion of DMSP into dimethylsulfoxide (DMSO). In this study, the potential loss of particulate organic matter to the dissolved phase through solubilization processes was estimated to be on average $10 \pm 5\%$ of the unpreserved trap material (traps deployed at 150 m, Pommier et al. 2008), indicating that our loss rates might be slightly underestimated. Turnover of *in situ* standing stocks of DMSP via the recycling of primary production through the microbial loop may also be an important loss process for DMSP during its descent through the water column. Matrai & Vernet's (1997) study of a senescent diatom population in the Barents Sea concluded that less than 5% of the particulate DMSP standing stock was removed from the upper mixed layer (14 to 65 m) during a 36 h period, which they attributed to strong recycling within the SML. On Days 2, 4 and 6 of the present study, the mean relative contribution of carbon from DMSP_p (C-DMSP_p) to the POC pool in the particle collectors (0.41%, data not shown) was slightly lower than the mean relative contribution of C-DMSP_p to the POC pool at the DCM (0.69%, data not shown), suggesting a possible preferential recycling of DMSP_p over POC. Furthermore, we estimated that the recovered fraction of DMSP_p within the traps explained between 5 and 18% of the loss of DMSP_p in the upper water column (0 to 75 m, Table 2). These results suggest that more than 80% of the total losses of DMSP_p between the surface and 75 m were due to processes other than sinking (i.e. autolysis, grazing, viral lysis). These results suggest that recycling through the food web dominated DMSP_p-consuming processes during our study, which is in accordance with measurements conducted during the decline of an iron-induced diatom bloom in the Gulf of Alaska. That study revealed that only a small proportion (18%) of the SML POC was lost due to sinking, and that most (69%) of the loss of POC from the SML was attributable to bacterial remineralization and mesozooplankton grazing (Boyd et al. 2004).

Rapid loss of DMSP_d

The decaying diatom bloom was associated with temporal variations in DMSP_d concentrations throughout the water column. On Days 1 and 2, a pulse of DMSP_d in the upper 75 m of the water column occurred, which was rapidly followed by a depletion of DMSP_d stocks (Fig. 3C). The higher concentrations of DMSP_d below the DCM during the first 2 d suggest that, prior to our sampling period, phytoplankton cells may have been less efficiently trapped at the DCM, resulting in the passive sinking of DMSP-containing cells and the release of DMSP below the nitracline. This observation is in agreement with the common

understanding of the collapse of diatom blooms, which are thought to sink out rapidly and release DOM during their descent in the water column (Parsons & Lalli 1988, Honjo & Manganini 1993). However, a very different pattern in the vertical distribution of pools of DMSP was observed over the following 5 d of our study (as discussed in the previous section). At 10 m, concentrations of DMSP_d were positively correlated with concentrations of total DMSP_p ($\tau = 0.71$, $p < 0.05$) as well as with concentrations of DMSP_p associated with the >20 μm class ($\tau = 0.71$, $p < 0.05$). This implies that the accumulation and loss of particulate and dissolved DMSP were tightly coupled in the SML and that the release of DMSP_p could have occurred through cell autolysis (Nguyen et al. 1988). The release of DMSP into the dissolved phase could also be attributable to viral lysis (Hill et al. 1998) as well as inefficient feeding and excretion by zooplankton (Dacey & Wakeham 1986), although no direct evidence of either of these processes is available. The increasing abundance of empty diatom frustules observed in the phytoplankton samples (S. Lessard pers. comm.) could suggest either one of these processes (autolysis, viral lysis or zooplankton grazing).

The rapid decline of the DMSP_d pool in the SML (Fig. 3C) coincided with the development of the bacterial assemblage (Fig. 2B), which was likely fuelled by the release of dissolved organic matter from the decaying diatom bloom (Pommier 2007). Bacteria associated with oceanic algal blooms are known to play important roles in sulfur cycling (Gonzalez et al. 2000) and tightly control the DMSP_d pool during phytoplankton blooms, with DMSP_d turnover times typically between 0.1 and 1 d (Kiene & Linn 2000). As observed during the collapse of a silicate-limited diatom bloom during a mesocosm study (Levasseur et al. 1996), the decline in concentrations of DMSP_d (Fig. 3C) suggests that bacterial uptake was an important loss process for the DMSP_d standing stocks in the upper layers of the water column. The overall negative net production rates of DMSP_d found in the upper ca. 45 m of the water column (Fig. 5B,E) supports this interpretation and further indicates that a strong recycling of DMSP_d was occurring. Furthermore, microbial DMSP_d consumption was at its highest in the SML on Days 1 and 2, and then diminished both in the SML and at the DCM on Days 3 to 7 (A. Merzouk unpubl. data). However, these lower DMSP_d consumption rates were sufficient to maintain DMSP_d concentrations in short supply from Day 4 onward (A. Merzouk unpubl. data) presumably throughout the water column (DMSP_d < 1.5 nmol l⁻¹ after Day 4 between 0 and 200 m). These results suggest that the rapid heterotrophic metabolism of DMSP prevented the accumulation of DMSP_d.

Rise in sea surface DMS and ventilation

The decrease in DMSP_p and DMSP_d concentrations in the SML was associated with an increase in DMS concentration in the upper 45 m of the water column. As the bloom declined, DMS concentrations moderately increased in surface waters (0 to 45 m) from 0.6 to 1.1 nmol l⁻¹ until Day 5, but remained lower and fairly stable (<0.6 nmol l⁻¹) below the DCM (45 to 200 m, Fig. 3D). The increase in surface concentrations of DMS is in accordance with studies observing peaks in DMS formation following the decline of phytoplankton blooms, although the relative magnitude of these increases varies widely in the literature. Namely, increases in DMS concentrations have been observed during the decline of a diatom bloom in the Barents Sea (Matrai & Vernet 1997), as well as in a mesocosm experiment (Nguyen et al. 1988). Elevated concentrations of DMS have been reported for blooms of *Phaeocystis* in the natural environment (Liss et al. 1994 and references therein), which were suggested to occur following mass release of DMSP_d at the decline of these blooms (Liss et al. 1994). Matrai & Keller (1993) also reported a maximum release of DMS during the senescence phase of a large *Emiliania huxleyi* bloom in the Gulf of Maine, while Leck et al. (1990) observed this phenomenon after the first peak of a spring bloom in the Baltic Sea. Although the wane of blooms is often associated with higher levels of DMS, highest concentrations of DMS have also been associated with the peak (Barnard et al. 1984) and exponential growth phase of blooms (Kwint & Kramer 1996, van Duyl et al. 1998), which does not permit us to exclude the occurrence of higher DMS concentrations prior to our study period. However, in the studies cited above, the enhancement of the transformation of DMSP_d to DMS has often been related to high DMSP-lyase activity known to be associated with certain bloom-forming phytoplanktonic groups such as *Phaeocystis* spp. (Stefels & van Boekel 1993). To our knowledge, DMSP-lyase activity has not been shown for the diatom species *Chaetoceros* spp. and *Thalassiosira* spp. that dominated the phytoplankton assemblage at the beginning of our study period. Mean DMS concentrations observed at 10 m during this study (0.9 ± 0.2 nmol l⁻¹) were lower than the climatological mean (4 nmol l⁻¹) from Kettle et al. (1999), but were in the same range as those reported in the North Atlantic Ocean during spring by Scarratt et al. (2002), Andreae et al. (2003) and Levasseur et al. (2004).

In situ net transformation rates of DMS, integrated over the first 10 m of the water column, displayed a significant increase (with the exception of the last day), consistent with the decay of the diatom bloom (Fig. 5C). To compare the net changes in DMS produc-

tion observed during this study with those previously reported, rates were measured at discrete depths (10 m and the depth of the DCM). The net DMS production rates at 10 m and at the DCM varied between -0.4 and $0.4 \text{ nmol l}^{-1} \text{ d}^{-1}$ (Table 3), falling into the range of estimated net DMS production rates in surface waters of different biogeochemical provinces in the northwest Atlantic during spring (Scarratt et al. 2000b, Levasseur et al. 2004). Net production rates of DMS remained low relative to a station investigated in the North Atlantic drift during May ($9.6 \text{ nmol l}^{-1} \text{ d}^{-1}$, Scarratt et al. 2000b), which, however, probably reflected the presence of a bloom of high DMSP-producing phytoplankton such as *Chrysochromulina* sp. The bacterial turnover of dissolved DMSP is thought to result in minor net production of DMS under certain conditions (Kiene & Linn 2000). Assimilation of DMSP-sulfur (i.e. demethylation) is typically the main bacterial degradation pathway for DMSP, particularly in environments rich in dissolved organic carbon (such as during the collapse of a diatom bloom) where bacterial requirements in sulfur are high (Kiene et al. 2000, Levasseur et al. 2004). Modifications in the type and the availability of substrate during the different stages of a bloom linked to changes in the composition and dynamics of the bacterioplankton assemblage are important factors in controlling bacterial pathways of DMSP degradation (Pinhassi et al. 2005). For instance, increases in bacterial productivity and sulfur demand during the development of a DOC-rich and DMSP-poor diatom bloom in the northeast Pacific Ocean resulted in the preferential demethylation of DMSP_d and in lower DMS production rates (Merzouk et al. 2006). In the present study, the fairly low net production rates of DMS (despite the high loss of DMSP_d) suggest that demethylation of DMSP_d was the dominant loss pathway for this compound. This conclusion is supported by sensitive sulfur radioisotope tracer studies (^{35}S -DMSP) (A. Merzouk unpubl. data). In terms of DMSP and DMS cycling, results observed in our Lagrangian study were similar to the post diatom bloom conditions encountered by Levasseur et al. (2004) at a Grand Banks station in the northwest Atlantic Ocean in spring. Although their study differed in the approach used (24 h *in situ* incubation versus 7 d Lagrangian study), they observed a net loss of DMSP_p from surface waters, a rapid recycling of DMSP_d by the microbial assemblage and low net production rates of DMS, and concluded that demethylation was an important sink for DMSP_d in these waters. These findings, together with our observations, highlight the fact that DMSP_d release during physiologically older blooms of diatoms, coupled to high bacterial abundance and requirements for sulfur, may lead to low DMS production.

Although we observed low levels of *in situ* net production rates of DMS, the increase in sea surface con-

centrations of DMS led to a significant increase in emission rates of DMS to the atmosphere (Fig. 6), which rose from 0.4 to $3.1 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ between Days 1 and 5 ($\tau = 0.80$, $p < 0.05$). The subsequent decrease in stocks of DMS in the SML also translated into a decrease of sea-to-air fluxes that fell below $0.7 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ on Days 6 and 7. Despite the mid-study increase, ventilation of DMS was fairly low during the study period and the mean sea-to-air flux calculated for the Lagrangian study ($1.5 \pm 1.1 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$) remains lower than the mean flux ($5.3 \pm 3.3 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$) estimated by Andreae et al. (2003) during spring in the North Atlantic using the Nightingale et al. (2000) parameterization. The fairly calm meteorological conditions encountered during the sampling period, along with moderate concentrations of DMS, most probably limited the ventilation of DMS from surface waters in the sampling area.

CONCLUSIONS

The timing of this cruise, together with the Lagrangian approach, provided a rare opportunity to obtain insight into the dynamics of DMSP and DMS during the declining phase of a spring diatom bloom in the northwest Atlantic Ocean. In so doing, it has allowed us to quantify and estimate daily variations, sink processes and fluxes between pools of DMSP and DMS and to address what controls these different transformation rates. The collapse of the diatom bloom coincided with the settling of pigmented material and DMSP_p out of the SML and their accumulation at the DCM. The decline of this bloom of large phytoplankton cells resulted in low DMSP_p export from the upper 75 to 100 m of the water column, with less than 2% of the standing stock being lost due to sedimentation. Pulses of DMSP_d in the SML during the first 2 d of the study were followed by the development of the bacterial community and the subsequent near-exhaustion of the DMSP_d pool. Despite a fast depletion of the DMSP_d pool, *in situ* net production rates of DMS were low, suggesting that demethylation dominated pathways of DMSP_d bacterial metabolism. In this study, we captured a large part of the decline of the diatom bloom. However, the sampling period was not long enough to describe the ultimate fate of the diatom population retained at the DCM. Whether these large phytoplankton cells are recycled *in situ* through the microbial loop, thus facilitating the potential turnover of phytoplanktonic DMSP into DMS, or whether they are massively exported to depth along with their DMSP content has important consequences for DMSP and DMS cycling. Assessing the importance of these processes is critical with respect to the influence and overall effect of the spring bloom on the biogeochemical cycling of DMSP and

DMS in the North Atlantic Ocean and its role in transferring DMS towards the atmosphere. Studies encompassing comprehensive information on food web structure and interactions, including heterotrophic activities and metabolism (zooplanktonic and microbial), should allow an improved understanding of the fate of DMSP and DMS in relation to the development and decline of spring blooms in temperate regions of the North Atlantic Ocean.

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