

Production and consumption of dimethylsulfide (DMS) in North Atlantic waters

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ABSTRACT: Production and consumption of dimethylsulfide (DMS) were studied in surface waters of the northwest Atlantic between latitude 32° and 45° N during May 1998. The kinetics of DMS production by the whole planktonic community were studied in short-term (3 h) experiments using additions of dissolved dimethylsulfoniopropionate (DMSP_d) (0 to 3000 nM). Measurements of DMS production and DMSP_d consumption showed that the DMS production rate increased in direct proportion to the concentration of added DMSP_d. This rate relationship did not saturate, suggesting acclimation of the microbial community to DMSP_d concentrations much higher than the average for bulk seawater. Longer-term experiments were performed in which DMSP_d consumption and DMS production were measured over 48 to 60 h. The DMSP_d consumption rate decreased as the concentration of DMSP_d decreased during the incubations. However, the DMS production rate was initially constant for the first 36 h. When DMSP_d concentrations fell below 50 nM, DMS production stopped, even though DMSP_d consumption continued. A possible explanation is that DMSP cleavage might dominate the total DMSP consumption at high DMSP_d concentrations while DMSP demethylation and other processes dominate at low DMSP_d concentrations. DMS consumption was measured both directly and by using the DMS consumption inhibitors dimethyl disulfide (DMDS) and methyl butyl ether (MBE). DMS consumption was generally undetectable except at 1 station dominated by a dense population of the DMSP-producing phytoplankton *Chrysochromulina* sp. and where ambient DMS concentrations were high. This suggests that the potential for DMS consumption is highest where ambient DMS levels are elevated. Pooling results from these experiments with earlier results from more northerly waters revealed an inverse exponential relationship ($r^2 = 0.75$, $p < 0.0001$) between the potential rate constant and chlorophyll *a* standing stock across a wide area of the Northwest Atlantic. This finding is potentially useful for the development of DMS production models.

KEY WORDS: Dimethylsulfide · DMS · Dimethylsulfoniopropionate · DMSP · Sulfur · Bacteria · North Atlantic

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INTRODUCTION

Dimethylsulfide (DMS) and its precursor, dimethylsulfoniopropionate (DMSP), along with dimethylsulfide (DMSO), form the major pool of organic sulfur in the marine environment. The production and transformation of these compounds comprise an important part of the sulfur cycle. DMS is readily oxidized in the atmosphere to form sulfate aerosols which are thought to be climatically important due to their ability to scat-

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ter sunlight and their role in the formation of cloud condensation nuclei. Both these processes increase the planetary albedo and exert a cooling influence on the climate. Charlson et al. (1987) have hypothesized that marine DMS production may act as a climate regulatory mechanism via a feedback loop involving surface ocean temperature, phytoplankton, DMS and sulfate aerosols. According to this hypothesis, warmer ocean temperatures resulting from global climate warming would stimulate processes leading to the production of DMS. The enhanced DMS release would lead to increased formation of sulfate aerosols and cloud condensation nuclei. Increased light scattering and cloud cover would exert a cooling effect on the climate, thereby counteracting the warming trend. The existence of this 'global thermostat' has not yet been confirmed, but there is evidence to support a relationship between DMS-derived sulfate aerosols and climatic events (Falkowski et al. 1992, Legrand 1997, Legrand et al. 1997, Clarke et al. 1998).

While phytoplankton are known to be the principal source of DMSP, bacteria are thought to provide the major mechanism for transforming DMSP to DMS in seawater (Kiene & Service 1991, Gabric et al. 1993, Ledyard & Dacey 1994, Wolfe 1996). The cleavage of DMSP to DMS and acrylate is accomplished enzymatically via DMSP-lyase which has been shown to exist in marine bacteria (Ledyard et al. 1993, de Souza & Yoch 1995a, Yoch et al. 1997). There are also a few species of phytoplankton which are known to possess DMSP-lyase (Stefels & Dijkhuizen 1996, Steinke et al. 1998), and it is speculated that there may be others. The relative contribution of phytoplankton to marine DMS production is presently unknown, but may be significant in regions where DMSP-lyase-containing algal species are abundant. A second major mechanism of DMSP degradation by bacteria is demethylation, which does not produce DMS. Although some bacterial isolates expressing both pathways have been isolated (Gonzalez et al. 1999), the bacterial assemblage responsible for demethylation appears to be generally distinct from that responsible for DMSP cleavage (Visscher et al. 1992). The ratio of DMSP cleavage to demethylation is variable and is often expressed as a DMS production yield, or the rate of DMS production relative to the total loss rate of DMSP. DMSP cleavage is generally thought to be the less significant of the 2 processes, and DMS production yields measured in marine waters fall typically between 5 and 30% (Kiene & Service 1991, Kiene 1992). There is some evidence that the yield may decrease as a phytoplankton bloom ages due to an increase in the relative importance of demethylation over DMSP cleavage (Kwint et al. 1996, van Duyl et al. 1998). In addition to bacterial DMS production, considerable bacterial consumption of DMS has been ob-

served by various authors (Kiene & Bates 1990, Kiene 1992, Kwint & Kramer 1995, Kwint et al. 1996, Wolfe et al. 1999). These investigations have shown the importance of bacteria in regulating DMS production. However, studies of the dynamics and transformations of DMSP and DMS have usually been conducted in specific geographic regions (e.g. Bates et al. 1994, Matrai & Vernet 1997) or specialized environments such as microbial mats (Jonkers et al. 1998). Little is known about the spatial and temporal variation of bacterial DMS production and consumption on oceanic scales. In particular, there is a lack of knowledge about the variation of this activity as a function of temperature. Although such a relationship might be inferred from the hypothesis of Charlson et al. (1987), few data exist to support this conjecture.

The present study had 2 major objectives. The first was to investigate DMS production and consumption processes (including potential DMS production rates) across a wide area of the temperate North Atlantic, extending between Nova Scotia, Bermuda and Newfoundland, in springtime. DMS production rates and rate constants were determined during short (3 h) incubations of surface seawater amended with a range of dissolved DMSP (DMSP_d) concentrations (up to 3000 nM). The second major objective was to investigate the dynamics of DMSP-to-DMS transformations, including rates and percentage yields, under conditions simulating the first 2 d following the decline of a bloom. Long-term incubations (48 to 60 h) were conducted in which DMS production and DMSP consumption were measured following the addition of a 100 nM pulse of DMSP_d. This concentration falls within the upper range observed in open-ocean waters (Malin et al. 1993, Palmer Locarnini et al. 1998), and corresponds with DMSP_d concentrations released following the decline of DMSP-producing phytoplankton blooms during mesocosm experiments (Kwint et al. 1996, Levasseur et al. 1996).

MATERIALS AND METHODS

The cruise track of May 1 to 17, 1998 (Fig. 1), was designed to traverse several water masses of different temperatures as defined by the biogeographic provinces of Longhurst (1995) (abbreviations in parentheses): Gulf Stream (GFST), North Atlantic Subtropical Gyre (NAST) commonly known as the Sargasso Sea, North Atlantic Drift (NADR) and the Northwest Continental Shelf (NWCS) including the Grand Banks. Surface-water temperatures encountered during this study ranged from 4 to 20°C. Stations were occupied in each of the 4 biogeographic provinces. Incubations were also performed at 2 additional stations, near the

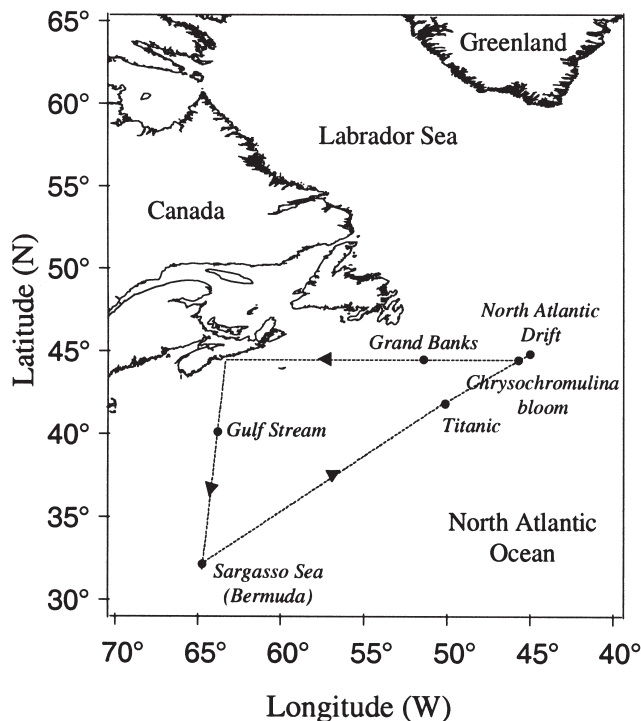


Fig. 1. Map of study area showing cruise track and locations of 6 sampling stations

Titanic wreck site and in a bloom of the prymnesiophyte *Chrysochromulina* sp. Not all types of experiments were performed at all stations. It should be noted that based on examination of the ship's continuous temperature log after the cruise, the Gulf Stream station was actually located slightly north of the stream itself. The Sargasso Sea fixed station was located at the Hydrostation S site of the Bermuda Atlantic Time Series (BATS) for which there is an existing time series of DMS data including 2 annual cycles (Dacey et al. 1998). At all stations, samples were collected with a rosette sampler equipped with 10 l Niskin bottles and a CTD which simultaneously measured salinity, temperature, pressure and chlorophyll fluorescence. Chlorophyll *a* (chl *a*) was determined fluorometrically after filtration (Whatman GF/F) and extraction into 90% acetone using the method of Parsons et al. (1984). Bacterial cell counts were performed on an epifluorescence microscope using formaldehyde-preserved samples filtered onto 0.2 μm Nuclepore membranes and stained with DAPI using the method of Porter & Feig (1980). Phytoplankton identification and enumeration was performed on formaldehyde-preserved samples using a settling column and inverted microscope.

All experiments were conducted using surface seawater collected by Niskin bottles at a depth of <5 m and screened through 202 μm Nitex mesh to remove large grazers. All pouring and mixing was performed

gently to avoid bubble formation which could alter the concentration of DMS. As it was filtered, the water was transferred to 10 l insulated containers from which it was dispensed into the incubation bottles. Incubation procedures were begun immediately following sample collection. The incubation bottles (250 ml brown polyethylene with screw caps) were cleaned by soaking in 10% HCl overnight followed by rinsing with deionized water. They were rinsed once with seawater, filled completely to eliminate any headspace, and incubated in the dark at ambient surface temperature in a flowing seawater incubator. In bottles containing amendments of DMSP_d and/or DMS consumption inhibitors (dimethyldisulfide and methyl butyl ether), the additions were made at the time of filling and the bottles gently inverted 3 times to mix the contents.

At each sampling point, 1 or 2 bottles of each treatment were mixed gently by slow inversion and then sampled for DMS and DMSP_d. Samples were prepared by filtering 80 ml from the incubation bottle through a 25 mm GF/F (Whatman) filter using gentle suction filtration (maximum vacuum 130 mm Hg). Although suction filtration may not be ideal, because of the potential for cell lysis on the filters, it was necessary to accommodate the high sample frequency (up to 12 bottles h⁻¹). The initial measured DMSP_d concentrations in the unamended bottles were elevated ca 50% over ambient levels during these experiments, possibly as a result of this effect. However, since the discrepancy probably arises during filtration, this should not affect the rates of DMSP consumption or DMS production in the incubations. DMS samples were prepared by carefully filling a 24 ml serum vial with filtrate and immediately sealing the top with a butyl rubber septum and aluminum crimp. The vials were filled as completely as possible to minimize the remaining headspace. Separate tests (unpublished) indicated that there is no significant loss of DMS in samples sealed with butyl septa compared to those with Teflon septa, even following storage for several hours. DMS samples were analyzed as quickly as possible, usually within a few minutes of collection. For DMSP_d samples, 23 ml of filtrate was decanted into a vial containing 1 ml KOH solution (10 N). In the case of samples which contained very high concentrations of added DMSP_d (500 nM and higher), only 1 ml of filtrate was used, with the remaining volume made up of 22 ml of deionized water plus 1 ml of 10 N KOH. Although there is some potential loss of DMS while decanting the sample into a vial already containing KOH, comparisons of this method with the injection of KOH into sealed sample vials revealed no significant difference in the measured DMSP_d concentrations (unpubl. data). Furthermore, the manipulation is simpler and it eliminates the risk of leakage through the pierced septum during storage.

DMSP samples were stored at 4°C for at least 24 h to allow the solution to react, and were analyzed within at most 4 wk of collection.

Analyses were performed using a pair of purge-and-trap systems each coupled to a Varian 3400 gas chromatograph (GC) using a modified version of the method of Leck & Bågander (1988) (see Cantin et al. 1996 for details of the method). One GC was fitted with a flame photometric detector (FPD), the other with a more sensitive pulsed-flame photometric detector (PFPD). The PFPD was used to analyze all the DMS samples and the more dilute DMSP samples. The FPD was used for the more concentrated DMSP samples. For the analysis of DMSP, the GCs were calibrated against a gravimetric standard of DMSP (50 ng ml⁻¹ in distilled water) prepared in 10 ml crimp vials containing 0.4 ml 10 N KOH. For the analysis of DMS samples, the GC was calibrated against microlitre injections of He containing approximately 17 ng ml⁻¹ of DMS. This was prepared using a permeation tube apparatus (Kin-Tek). The analytical method has a precision of ca 10% and a minimum quantification limit for both DMS and DMSP_d of ca 0.08 nM.

Three types of experiments were performed:

Short-term incubations—kinetic rate determinations. These experiments were based on the methods of Ledyard (1993) and Schultes et al. (2000). Briefly, 28 water samples (250 ml) were incubated for up to 3 h with a series of added DMSP_d concentrations (0, 50, 100, 500, 1000, 2000 and 3000 nM). At Time 0 and after each hour, 1 bottle at each DMSP_d concentration was filtered and analyzed for DMS and DMSP_d. For each initial DMSP_d concentration, the average DMS production rate (nmol l⁻¹ h⁻¹) over the 3 h experiment was determined from the linear regression of DMS concentration versus time. A rate constant (*k*) was calculated for each experiment by plotting the DMS production rate vs initial DMSP_d concentration and determining the slope. Since the experiments are conducted using the natural microbial assemblage (including phytoplankton), and rely on additions of DMSP_d, the measured rates are potentials which apply to the entire assemblage, not simply to bacteria. The rate constant is thus a 'community potential' rate constant (hereafter abbreviated *k*_{pot}) which is effectively an index of the potential for DMS production by the microbial community following a pulse of DMSP_d. This experiment was performed at 5 stations: Gulf Stream, Sargasso Sea, Titanic, North Atlantic Drift and Grand Banks.

Long-term incubations. At 4 stations (Gulf Stream, Sargasso Sea, North Atlantic Drift and Grand Banks), the incubation procedures were extended to allow determination of the dynamics of DMSP and DMS over longer timescales, including whether the DMS production rates observed in short-term incubations could be

sustained for more than a few hours. The control (0 nM added DMSP_d) and 100 nM added DMSP_d treatments were extended to include duplicate samples at 6 to 12 h intervals over 48 to 60 h. The principal objective was to determine both the endogenous rates of DMSP_d consumption and DMS production over ≥48 h as well as the potential rates following a 100 nM pulse of DMSP_d. Another objective of the long-term experiments was to measure bacterial DMS consumption rates using chemical inhibitors to prevent the bacterial consumption of DMS. By measuring the rate of DMS production with and without inhibitors, the rate of bacterial DMS consumption can be calculated from the difference. This method has been employed by other authors using a variety of chemical inhibitors (Kiene 1990, 1992, Visscher & Taylor 1993, Wolfe et al. 1999). In this study, dimethyldisulfide (DMDS) and methyl butyl ether (MBE) were used as specific inhibitors of bacterial DMS consumption (Visscher & Taylor 1993, Wolfe & Kiene 1993). They were added to the incubation bottles at final concentrations of 200 nM and 30 μM for DMDS and MBE, respectively. The inhibitors were added to bottles both with and without the 100 nM DMSP_d amendment. Although the precise mechanism of inhibition has not been described, isotopic tracer studies using ³⁵S suggest that DMDS does not inhibit DMSP demethylation (R. P. Kiene pers. comm.), and therefore should not interfere with measurements of DMSP consumption. Measurements were taken at the same intervals as for the control and 100 nM DMSP_d treatments. Because of limitations in the rate of sample processing and analysis, a maximum of 6 different treatments could be used in each experiment. At all stations these included a control with no additional DMSP_d and a 100 nM DMSP_d treatment. Thus, for a typical long-term experiment the 6 treatments were: (1) control (no addition); (2) 100 nM DMSP_d; (3) control + DMDS; (4) 100 nM DMSP_d + DMDS; (5) control + MBE; (6) 100 nM DMSP_d + MBE. With duplicate bottles for each treatment, 12 bottles were sampled at each time point for a total of 24 samples (12 each of DMS and DMSP_d). Note that the MBE treatments were omitted at the Sargasso Sea station.

DMS consumption. To verify the results of the inhibitor experiments, a second method of measuring DMS consumption was developed employing direct additions of DMS to seawater. A gas stream (DMS in He) at a concentration of approximately 17 ng DMS ml⁻¹ was prepared using a permeation tube. One hundred ml of this gas was injected into a 1 l Tedlar gas sampling bag (Chromatographic Specialties) containing approximately 600 ml of gravity-filtered surface seawater (2 μm GMF glass-fibre filter, Whatman) to yield a final concentration of approximately 50 nM DMS. The bag was agitated gently and kept in the

dark at room temperature for approximately 1 h to allow it to reach equilibrium. The water was then transferred via syringe into ten, 30 ml crimp-sealed vials and incubated in the dark at ambient surface seawater temperature. By pre-filtering the seawater through a 2 μm filter, the intention was to remove most of the phytoplankton while allowing most of the free-living bacteria to remain in the sample. This method was employed to allow direct injection of the samples into the purge/trap apparatus without the risk of introducing phytoplankton cells and detritus which could contaminate the apparatus with DMSP. The possible limitation of this approach is that any bacteria associated with particles or phytoplankton cells which may have been present in the sample were probably removed during the filtration step. It is not known whether this could affect the measured DMS consumption rates. Duplicate bottles were analyzed for DMS concentration at $t = 0$ and at approximately 12 h intervals thereafter for 48 h. A parallel series of bottles containing only filtered seawater (no added DMS) were analyzed as a control. Experiments of this type were performed in the Sargasso Sea, the North Atlantic Drift and the *Chrysochromulina* sp. bloom station.

RESULTS

Characteristics of the sampling stations

Table 1 describes the 6 stations where experiments were conducted. Water salinity, temperature, and the *in situ* concentrations of chl *a*, bacteria, DMS, DMSP_d

and particulate DMSP (DMSP_p) are given as well as the dominant phytoplankton species. The *Chrysochromulina* sp. bloom station stands out as having the highest concentrations of DMS, DMSP_p and bacterial cells. At this station, the population of *Chrysochromulina* sp. in the surface water was approximately 4×10^5 cells l^{-1} . By comparison the other stations had much lower phytoplankton populations. The Gulf Stream station had a mixed population of flagellates (ca 1.5×10^5 cells l^{-1}). The Sargasso Sea and North Atlantic Drift stations were dominated by the naked dinoflagellates *Gymnodinium* sp. and *Gyrodinium* sp. (1 to 2×10^5 cells l^{-1}). The Titanic station was dominated by a sparse population of *Chaetoceros* sp. (7×10^4 cells l^{-1}) while the Grand Banks displayed a mixed population of cryptophytes (1×10^5 cells l^{-1}).

Short-term experiments

Fig. 2A shows the results of a typical short-term experiment, in this case at the Sargasso Sea station. Production of DMS proceeded in a linear fashion for at least 3 h after the addition of DMSP_d. The slopes of the DMS curves (the potential DMS production rates) increase in direct proportion to the concentration of added DMSP_d, although only at DMSP_d concentrations of 500 nM or more were the slopes significantly different from zero (Student's *t*-test, $p \leq 0.05$). Similar results were obtained at the other 4 stations. Fig. 2B shows the DMSP_d concentrations during the course of a typical short-term experiment. The slopes were not significantly different from zero, and hence show no clear

Table 1. Characteristics of sampling stations showing oceanographic province (GFST: Gulf Stream; NAST: North Atlantic Sub-tropical Gyre; NADR: North Atlantic Drift; NWCS: Northwest Continental Shelf [as defined by Longhurst 1995]); salinity, water temperature, incubation temperature, and *in situ* concentrations of chlorophyll *a*, bacteria, DMS, DMSP_d, DMSP_p and dominant phytoplankton taxa. All samples were taken at a depth of <5 m. Bottom row: experiments performed at each station (ST: short-term; LT: long term; C: DMS consumption)

	Gulf Stream	Sargasso Sea	North Atlantic Drift	Grand Banks	Titanic	<i>Chrysochromulina</i> bloom
Oceanographic province	GFST	NAST	NADR	NWCS	NWCS	NADR
Salinity	35.9	36.5	35.9	32.9	32.7	35.8
Surface temp. ($^{\circ}\text{C}$)	18.2	20.2	15.3	3.1	4.2	14.4
Incubation temp. ($^{\circ}\text{C}$)	19	20	16	6	7	14.5
Chl <i>a</i> ($\mu\text{g l}^{-1}$)	0.85	0.10	0.62	0.26	0.25	0.52
Bacteria (10^9 cells l^{-1})	0.15	0.22	0.34	0.58	0.22	1.6
<i>In situ</i> DMS (nM)	0.3	2.2	2.3	0.3	1.0	4.3
<i>In situ</i> DMSP _p (nM)	11.7	21.7	30.2	39.4	8.5	78.9
<i>In situ</i> DMSP _d (nM)	3.2	5.4	12.4	6.4	3.1	7.7
Dominant phytoplankton	Flagellates	<i>Gymnodinium</i> sp. and <i>Gyrodinium</i> sp.	<i>Gymnodinium</i> sp. and <i>Gyrodinium</i> sp.	Mixed Cryptophyceae	<i>Chaetoceros</i> sp.	<i>Chrysochromulina</i> sp.
Experiments	ST, LT	ST, LT, C	ST, LT, C	ST, LT	ST	C

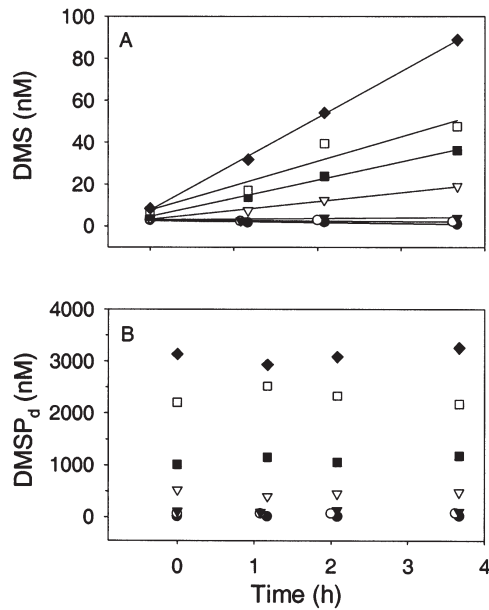


Fig. 2. Results of typical short-term incubation (kinetics experiment) at Sargasso Sea station. (A) Production of DMS (continuous lines indicate least-squares fit); (B) changes in DMSP_d following amendment with DMSP_d at 6 different concentrations. DMSP_d amendment key: (●) 0 nM; (○) 50 nM; (▼) 100 nM; (▽) 500 nM; (■) 1000 nM; (□) 2000 nM; (◆) 3000 nM

trend over the 3 h experiment. DMSP_d will be discussed in more detail in the context of the long-term experiments where the changes were significant and trends can be more easily discerned.

Using the slopes of the DMS curves from Fig. 2A, a kinetic curve can be constructed by plotting the potential DMS production rates against the concentrations of added DMSP_d. Fig. 3 shows such curves for 5 stations. Note that different vertical scales are used in each graph to provide the best resolution. While the 95% confidence interval bars on the rate estimates are in some cases large, and some of the rates are not statistically significant, it is important to remember that each rate determination is based on 4 independent samples, each incubated for a different interval. Notwithstanding that some rate determinations were not significant, all points fall very close to the least-squares line and have therefore been included in the regression to determine the potential rate constant k_{pot} (simply the slope of the line). No evidence of saturation was observed over the concentration range tested. In Fig. 4, k_{pot} is plotted relative to 4 variables which might be expected to influence potential DMS production: incubation temperature, chl *a* (as an index of phytoplankton standing stock), DMSP_p (an index of the standing stock of DMSP-producing phytoplankton) and bacterial counts. Fig. 4A shows the relation-

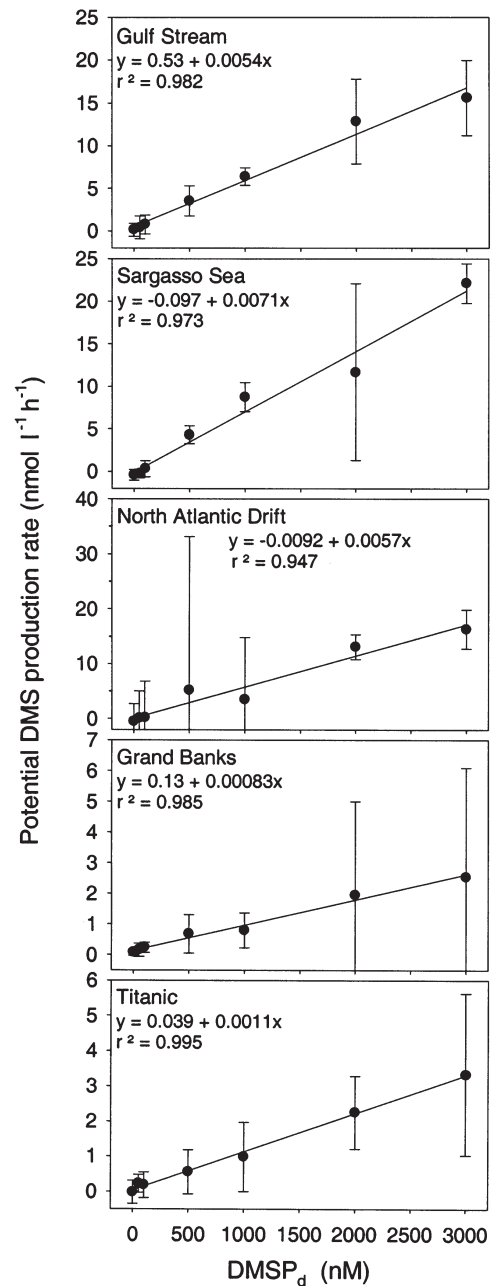


Fig. 3. Kinetic plots from short-term incubations at 5 stations. Potential DMS production rate versus initial DMSP_d concentration. Error bars: 95% confidence intervals of each rate determination; continuous lines: least-squares linear fit

ship between k_{pot} and incubation temperature. The data show that warmer temperatures were associated with higher rate constants in an apparently linear relationship. However, there is a large gap in the data between 7 and 16°C, so a truly linear trend is not certain. Fig. 4B, C & D reveal no significant relationships between k_{pot} and chl *a*, DMSP_p or bacterial cell counts.

Long-term incubations

Fig. 5A shows DMSP_d concentrations during the 60 h incubation at the Sargasso Sea station. For clarity, only the control and 100 nM DMSP_d treatments are shown.

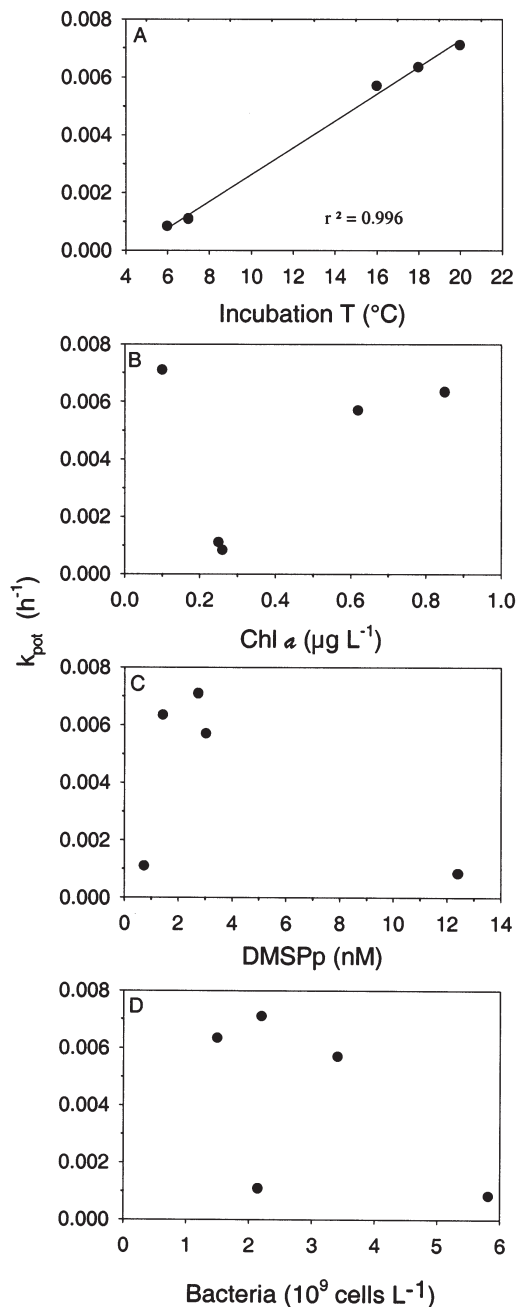


Fig. 4. Results of kinetic experiments at 5 stations showing relationships between potential rate constants (k_{pot}) and other oceanographic variables. (A) Incubation temperature; (B) chlorophyll *a* concentration; (C) DMSP_p concentration, (D) bacterial abundance

The corresponding inhibitor treatments followed very similar patterns. In both the control and the 100 nM treatment, DMSP_d underwent little net change in the initial 12 h, although the concentrations appeared to fluctuate about the mean. At some stations (the Gulf Stream and the control bottles at Sargasso Sea and the Grand Banks), DMSP_d actually increased during the initial 12 to 24 h before declining. Possible reasons for these variations are discussed below. After this initial increase, net DMSP_d consumption proceeded rapidly and the DMSP_d concentrations declined quickly over the remainder of the experiment. At none of the stations was the added DMSP_d completely exhausted by the end of the incubation. The post-lag rate of DMSP_d consumption was initially high and decreased as the concentrations diminished. Fig. 6A shows the average post-lag DMSP_d consumption rates for the controls and 100 nM added DMSP_d treatments at all 4 stations. The consumption rate in the controls was highest in the North Atlantic Drift ($1 \text{ nmol l}^{-1} \text{ h}^{-1}$) and much lower at the other 3 stations (0 to $0.2 \text{ nmol l}^{-1} \text{ h}^{-1}$). In the DMSP_d -amended treatments, the consumption rates also varied greatly, and again showed the highest rate in the North Atlantic Drift ($2.3 \text{ nmol l}^{-1} \text{ h}^{-1}$) and the lowest rates on the Grand Banks ($1.3 \text{ nmol l}^{-1} \text{ h}^{-1}$).

Fig. 5B shows the DMS production curves for the control and DMSP_d -amended (100 nM) bottles at the Sargasso Sea station. As with the DMSP_d curves, there

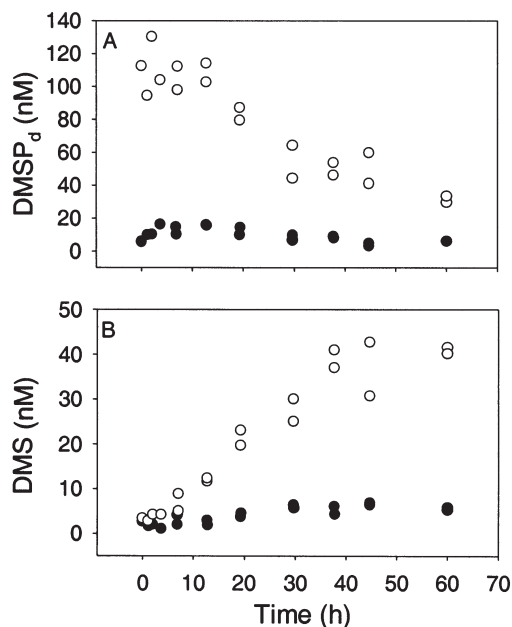


Fig. 5. Results of long-term incubation (Sargasso Sea station): (A) DMSP_d concentration; (B) DMS concentration. (●) control; (○) 100 nM added DMSP_d

appeared to be a slight lag in DMS production for the first few hours of the incubation. However, this lag was observed only at the Sargasso Sea station and may not be a general feature of such incubations. Following this lag, DMS production proceeded in a linear fashion for approximately 40 h after the DMSP_d addition. DMS accumulated steadily in the control bottles, indicating that there was a small net production of DMS in unamended samples. DMS production in the DMSP_d-amended samples was much faster than in the controls, and by the end of the experiment the DMS concentration had stabilized, indicating that net DMS production had ceased. This plateau was observed at all stations except the Grand Banks. Average DMS production rates (over 40 h) for the controls and 100 nM added DMSP_d treatments are shown in Fig. 6B. The error bars indicate the 95% confidence interval of each rate.

In the long-term incubations with 100 nM added DMSP_d, the highest potential rates of both DMSP_d consumption and DMS production were observed in the North Atlantic Drift while the lowest rates were observed on the Grand Banks (Fig. 6). The rates measured in the DMDS and MBE treatments are not shown, but no significant differences were seen between treatments which contained inhibitors and those which did not ($p > 0.05$). This indicates that DMS con-

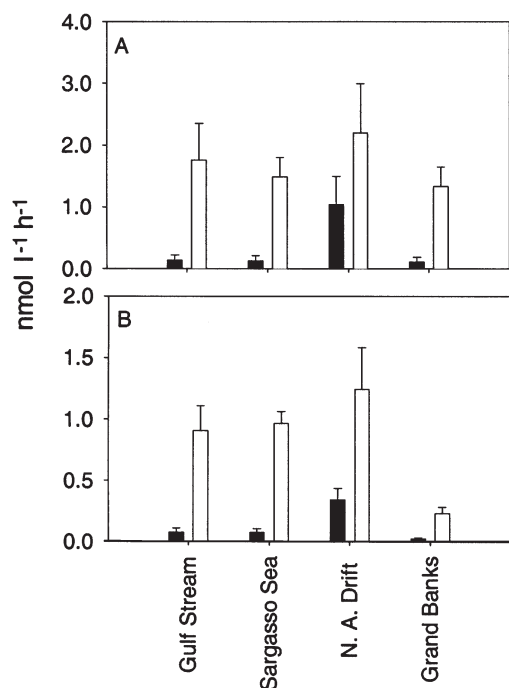


Fig. 6. Results of long-term incubations at 4 stations. (A) Net DMSP_d consumption rate; (B) net DMS production rate. Black bars: controls; open bars: 100 nM added DMSP_d treatments; error bars: 95% confidence interval of each rate (11 ≤ n ≤ 18)

sumption was undetectably low relative to the precision of the analyses. The implication of this is that the net DMS production rates measured here may in fact be insignificantly different from the gross production rates. Losses due to photooxidation are excluded, since the incubations were performed in the dark.

DMS consumption experiments

The DMS consumption experiments using the direct addition method were performed at 3 stations: Sargasso Sea, North Atlantic Drift and *Chrysochromulina* sp. bloom (Fig. 7A). The results indicate that significant bacterial consumption of DMS was observed only at the *Chrysochromulina* sp. bloom station. Furthermore, rapid DMS consumption was apparent only in the sample with added DMS (60 nM). The net consumption rate in the control bottles was near zero at all 3 stations. Fig. 7B shows bacterial counts for all the stations in this study. The *Chrysochromulina* sp. bloom station displayed an exceptionally high bacterial abundance, which was accompanied by a high DMS consumption rate.

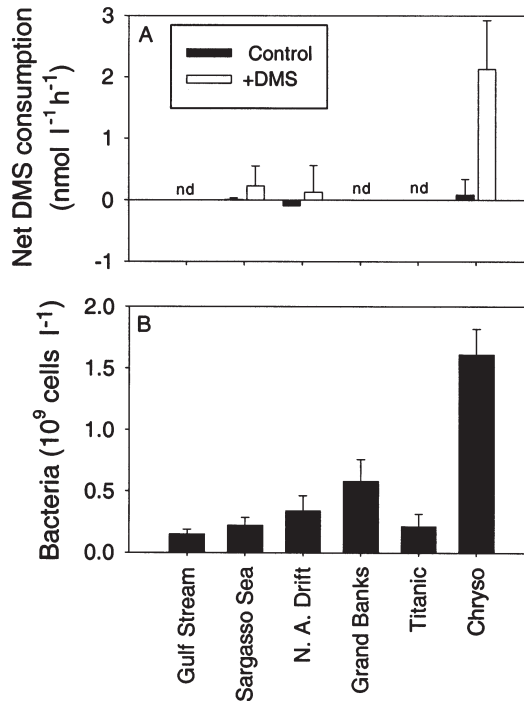


Fig. 7. (A) DMS consumption rate in unamended and amended (60 nM DMS) 2 μm filtered seawater samples; error bars: 95% confidence interval of each rate (n = 10). nd: no data. (B) Bacterial abundance for all stations; error bars: SDs of mean of 20 microscope fields. Chryso: *Chrysochromulina* sp.

DISCUSSION

Short-term kinetics of DMS production

Since all the rates and rate constants determined in these experiments are based upon amendments of DMSP_d, they must be regarded as potential rates, and might not reflect the actual *in situ* rates in unamended seawater. However, the striking linearity of the kinetic plots, even at amendments of 50 and 100 nM DMSP, suggests that the relationships found here are applicable to lower (and possibly higher) concentrations. At all stations, net production of DMS by the microbial community was clearly dependent upon the concentration of added DMSP_d, with apparently linear (substrate-limited) kinetics. None of the 5 experiments showed any signs of saturation at high DMSP_d concentrations. This is consistent with results from pure bacterial cultures which are known to have half-saturation constants (K_m) for DMSP cleavage in the micromolar range (Ledyard & Dacey 1994, de Souza & Yoch 1995b). Purified DMSP-lyase from the bacterium *Alcaligenes* sp. has a $K_m = 2$ mM (de Souza & Yoch 1995a). Thus it is clear that DMSP cleavage activity in marine bacteria remains unsaturated at concentrations which far exceed the normal ambient levels of DMSP_d in the water column (global mean monthly average DMSP_d = 18.1 nM, SD = 32.4 nM; Kettle et al. 1999). Ledyard & Dacey (1994) speculated that this might indicate that bacteria are adapted to high DMSP_d concentrations such as might be found in close association with cells and particles. This is supported by the observation by Cantin et al. (1999) that high potential rates of DMS production are associated with the particulate fraction in natural seawater samples. Microenvironments of high dissolved organic carbon concentration are postulated to exist around phytoplankton cells and in aggregates of marine snow (Azam & Ammerman 1984, Mitchell et al. 1985, Bowen et al. 1993, Blackburn et al. 1998). Although the conjecture that bacteria can effectively exploit such microenvironments is based more on modelling than direct observation (Bowen et al. 1993, Blackburn et al. 1997), some authors have speculated that such behaviour could explain the very high K_m values which have been observed for the bacterial uptake of various organic compounds, including glucose (Azam & Hodson 1981, Nissen et al. 1984). The possibility also exists that non-saturating kinetics could result from a low-affinity membrane-transport system, perhaps not even specific to DMSP_d, or indeed from simple diffusive transport across the cell membrane as suggested by Logan & Fleury (1993). However, there have been some reported observations of saturated DMS production kinetics in seawater under certain conditions (Ledyard & Dacey 1996, Scarratt et

al. 2000), which supports the existence of an enzymatic mechanism. Regardless of the actual mechanism involved, the unsaturability of DMSP cleavage at the DMSP_d concentrations typically measured in bulk seawater means that the potential DMS production following a phytoplankton bloom is limited only by the amount of DMSP_d released.

The observation of non-saturating kinetics across 4 different water masses and a wide range of temperatures indicates that this may be a general response in marine waters. However, there is evidence that bacterial DMSP cleavage can be saturated under some conditions. For example, in an earlier field study, Ledyard & Dacey (1996) found linear DMSP cleavage kinetics with no detectable saturation in seawater samples collected in the Sargasso Sea, but reported saturation in samples from coastal waters ($28 \text{ nM} \leq K_{m(\text{app})} \leq 575 \text{ nM}$, depending on the season). They also noted possible seasonal differences in the Sargasso Sea, with saturable kinetics observed in winter ($K_{m(\text{app})} = 20 \text{ nM}$), but not in autumn or spring. Such variations in DMS production kinetics could be dependent on the species composition of the microbial assemblage found at specific times of the year. It is known that certain taxa of marine bacteria possess DMSP-lyase activity while others do not (Ledyard et al. 1993), and that the composition of bacterial assemblages varies with bloom age and grazing pressure among other factors (Šimek et al. 1997, Kuennis 1998). The presence or absence of phytoplankton containing DMSP-lyase is another potentially important factor. The $K_{m(\text{app})}$ of the community is likely to be influenced by the presence of algal DMSP-lyases, and might vary with the species of phytoplankton involved.

The data from the 5 short-term experiments show a strong relationship between k_{pot} and the incubation temperature. Since k_{pot} is an index of the potential for DMS production by the planktonic community, this could represent either the direct effect of temperature on microbial activity or an indirect effect wherein water masses with different characteristics contain different populations of bacteria and phytoplankton. Such mechanisms, if real, could help support the 'global thermostat' hypothesis of Charlson et al. (1987). Changes in global ocean temperature which affect microbial populations could alter the distribution and rates of DMS production in surface waters. However, the 5 experiments shown here reveal no direct relationship between k_{pot} and phytoplankton biomass, measured as either chl *a* or DMSP_p. This further reinforces the conclusion that marine waters have a large potential for DMS production, even in areas where *in situ* DMS and DMSP production are normally low. The observation that the potential rate constant shows no direct relationship with bacterial abundance could

be related to 2 factors. Firstly, it is likely that only a minority of the bacterial population is actively producing DMS. For example, Visscher et al. (1992) found in the Caribbean Sea that DMSP-utilizing bacteria comprise only 10% of the total bacterial population, and only a subset of those produce DMS. Secondly, if algal DMSP-lyases make a significant contribution to the overall DMSP-lyase activity in seawater, then the potential rate constant will not necessarily be correlated with bacterial biomass.

Long-term changes in DMS and DMSP_d

The 4 long-term experiments allowed the resolution of changes in the relative concentrations of DMS and DMSP_d, and can provide some insight into the time-scale and efficiency of the cleavage mechanism.

After an initial period of stable or increasing concentrations, DMSP_d declined quickly and at some stations was almost completely depleted by the end of the experiment. As the DMSP_d concentration diminished, the consumption rate also declined, indicating that this rate is concentration-dependent. Note that this consumption is the net decrease in DMSP_d, and therefore includes changes resulting from all microbial uptake (cleavage, demethylation, microbial oxidation, intracellular storage, etc.) as well as production of DMSP_d by the phytoplankton in the sample. The initial increase in DMSP_d concentration in the first few hours was observed at 3 stations (Gulf Stream, Sargasso Sea and Grand Banks), both in controls and in DMSP_d-amended bottles. In 1 case (Sargasso Sea), an accompanying lag in DMS production was also observed. It is possible that an acclimation period of several hours is needed before the microbial community can begin to use a new source of DMSP_d. However, this lag period was not observed in all long-term incubations, nor was it observed in the higher-concentration treatments (DMSP_d ≥ 500 nM) of the short-term incubations. An alternative explanation is that the initial variations in DMSP_d concentration could be the result of phytoplankton cell lysis or leakage immediately following the start of the incubation. These processes could have been induced either as the result of stress caused by handling the samples or as a result of grazing by microzooplankton which would have been present in the samples. They may also represent an artifact introduced during the vacuum filtration which could liberate DMSP from cells. However, the generally good repeatability of the duplicate measurements later in the incubations suggests this was probably not the case. None of these possibilities can be confirmed in the absence of particulate DMSP determinations and cell counts or chlorophyll measurements during the incubations.

With the possible exception of the Sargasso Sea station, where the initial lag period was observed, DMS production proceeded in a linear fashion for approximately 40 h following the initial 100 nM pulse of DMSP_d. This suggests that no significant changes occurred in the bacterial population during this time period which affected its ability to utilize DMSP_d or DMS. Specifically, enzyme induction does not appear to be a factor. At the Grand Banks station, DMSP_d did not become greatly depleted, and DMS production, although slow, continued until the end of the incubation. However, at the other 3 stations (Gulf Stream, Sargasso Sea and North Atlantic Drift) the added DMSP_d became substantially depleted (< 50 nM) and the rate of DMS production declined to zero, although the DMSP_d pool was not completely exhausted. Furthermore, DMSP_d consumption continued (although at reduced rates) well after DMS net production had stopped. The simplest explanation for this is that the rate of DMS consumption may have increased toward the end of the incubation as the DMS concentration increased. Net DMS production would appear to slow down while DMSP_d consumption continued. However, this scenario is refuted by the results of the treatments containing competitive inhibitors where no DMS consumption could be detected. Net DMS production stopped, even in the presence of DMDS and MBE. A more plausible explanation is that other DMSP_d-consuming processes (including demethylation, biological oxidation or intracellular DMSP storage) dominate over the DMSP cleavage pathway at low DMSP concentrations. As the DMSP concentration decreased, the cleavage process would cease but DMSP uptake would continue. For example, in both mesocosms and in coastal waters, the relative importance of demethylation has been observed to increase during the declining phase of a phytoplankton bloom, as the DMSP_d becomes exhausted (Kwint et al. 1996, van Duyl et al. 1998). It has been shown, based on ³⁵S tracer studies (R. P. Kiene pers. comm.), that at low DMSP_d concentrations the bacterial community requires all of the DMSP to satisfy its sulfur demand, and so demethylation processes dominate. At higher DMSP_d concentrations where there is a surplus of sulfur, DMSP may be utilized simply as a carbon source and therefore the cleavage pathway becomes more significant. Visscher et al. (1992) reported that the DMSP-demethylating bacteria form a distinct population from the DMSP-cleavers but that does not exclude the possibility that the relative proportions or activities of the 2 groups might vary depending on the DMSP_d concentration. It should be noted that in a recent study (Gonzalez et al. 1999), several strains of the *Roseobacter* group were isolated which exhibited both pathways, although the authors concluded that this dual-pathway trait was probably rare.

It is the relative rates of cleavage and demethylation which determine the net yield of the DMSP to DMS conversion. This yield was calculated by comparing the DMS production to the rate of DMSP consumption. Averaged over the initial 40 h of the incubations, the ratio of the rate of DMS production to DMSP consumption in the samples amended with 100 nM DMSP_d was typically in the range of 30 to 60 % (mean = 45 %), indicating that the DMS production process in these experiments is relatively efficient. The values were generally lower in the unamended samples (mean = 35 %), but the difference was not statistically significant ($p > 0.05$, $n = 11$). However, a relationship between DMS yield and DMSP_d concentration has been observed in other studies (Gonzalez et al. 1999, Scarratt et al. 2000). In the present study, the lowest yields were observed at the Grand Banks station, which could be related to the low water temperature in that location compared to the other stations. While other authors have cited DMS production yields of <30 % and in some cases <10 % (Kiene & Service 1991, Kiene 1992), it appears that in the North Atlantic, as much as half of the added DMSP_d may be converted to DMS. However, this represents the net yield, and could reflect the low DMS consumption rates rather than any difference in the inherent efficiency of the DMSP-lyases in these samples. In an environment where DMS consumption was rapid, one would expect the overall net yield to be lower. It could also represent the effects of phytoplankton DMSP-lyases, since the incubations do not exclude phytoplankton. Similarly high net yields (exceeding 50 %) were recorded by Kwint et al. (1996) in a mesocosm system containing *Phaeocystis* sp., which is known to possess DMSP-lyase. However, neither of the 2 species known to possess this enzyme (*Phaeocystis* sp. and *Emiliania huxleyi*) were present in significant numbers at any of our stations, although the presence of dinoflagellates at 2 stations is a factor to consider since at least 1 species of *Gyrodinium* has been reported to show DMSP-lyase activity (Ishida 1968). If the overall conversion efficiencies measured here are representative of the open ocean, at least where the DMSP_d concentration is high, it implies that the potential biological supply of DMS to the marine atmosphere could be more significant than might otherwise be supposed. It has been generally assumed that the vast majority of DMSP is degraded to other compounds such as 3-mercaptopropionate and methanethiol, and that most of the DMS which is produced is cycled within the water column. However, these experiments show that there could be situations where DMS production is high while DMS consumption is very low. Thus, substantial amounts of DMS may be available to be ventilated to the atmosphere, although the actual rate of ventilation will also depend on wind

speed and water temperature, among other factors (Wanninkhof 1992, McGillis et al. 2000).

DMSP_d consumption and DMS production in controls

The rates of DMSP_d consumption and DMS production in the control bottles of the long-term incubations give an approximation of the *in situ* rates in the water column, and are therefore central to any understanding of the importance of these processes in a given region. The net rates of both DMSP_d consumption and DMS production in the control incubations were generally very low, and in some cases were indistinguishable from zero. Since these are net rates, this suggests that biological production and consumption of these compounds were nearly balanced in the surface waters. The exception was the North Atlantic Drift station, where significant net rates of DMSP_d consumption and DMS production were measured (ca 1.0 and 0.3 nmol l⁻¹ d⁻¹ respectively). This indicates that production and consumption of DMSP_d and DMS were not balanced at this station. This could be the result of DMSP consumption arising from DMSP_d released by cell lysis during preparation and handling of the samples. Indeed, the initial DMSP_d concentration in most of these incubations was higher than the *in situ* concentrations (ca 50 %). This effect was especially pronounced in the North Atlantic Drift, where the *in situ* DMSP_p concentrations were relatively high (ca 30 nM), which tends to support the DMSP-release hypothesis. This is likely to be related to the species composition of the plankton community at that location, which was dominated by the dinoflagellates *Gymnodinium* sp. and *Gyrodinium* sp., both of which are known to produce DMSP (Keller et al. 1989). Since (as mentioned previously) *Gyrodinium* sp. may possess DMSP-lyase, DMS production may be further enhanced.

DMS consumption rates

DMS consumption in these incubations was undetectable using the inhibitor method. Since the net DMS production rates in unamended samples were also relatively low, this observation fits generally with those of Wolfe et al. (1999), who observed a direct correlation between the rates of DMS consumption and DMS production. As an independent test of the validity of these results, direct additions of DMS to water samples were also made at the Sargasso Sea and North Atlantic Drift stations, and produced similarly negligible consumption rates. It can therefore be safely concluded that the *in situ* DMS consumption rates at those 2 stations were

indeed negligible and, by extension, it is reasonable to conclude that the undetectable DMS consumption rates in the other 2 long-term experiments are valid. Assuming that these stations were representative of their respective water masses, the implication is that bacterial DMS consumption is low across this part of the ocean at this time of year. Even when substantial quantities of DMS were introduced to the samples, the bacterial community could not consume DMS directly. Only at 1 station (the *Chrysochromulina* sp. bloom) was any consumption measurable, and then only in the DMS-amended samples. *Chrysochromulina* sp. is a known producer of DMSP (Keller et al. 1989), and possibly DMS as well, since other prymnesiophytes are known to possess DMSP-lyase. Its presence in the water column was accompanied by relatively high ambient levels of DMSP_p (79 nM) and DMS (4.3 nM) compared with the surrounding stations. The bacterial cell population was also high at this station compared to the others. It is possible that the potential for bacterial consumption of DMS is elevated in waters where the ambient concentration of DMS is high. This could be explained if the induction period for bacterial DMS consumption were longer than the time-scale of these experiments. Bacterial populations which were adapted to high ambient DMS concentrations would therefore show measurable DMS consumption rates while bacteria from DMS-poor waters would show negligible rates.

Relationship between potential rate constants and chl *a*

To test whether the strong relationship between the potential rate constant (k_{pot}) and incubation temperature shown in Fig. 4A can be extrapolated to a wider geographic area, the data from this study were pooled with determinations of k_{pot} made in the more northerly waters of the Labrador Sea (48° to 62°N) at approximately the same time of year using the same methodology (Schultes et al. 2000). Fig. 8A shows that the pooled data display no direct relationship between k_{pot} and incubation temperature, and thus the relationship of Fig. 4A does not hold across a wider geographic range. In Fig. 8B, the pooled estimates of k_{pot} are plotted against the concentration of chl *a*. In contrast to the limited data set of Fig. 4B, the pooled data show a significant relationship between k_{pot} and chl *a*, in which k_{pot} increases with increasing chl *a* concentration and reaches a maximum above 2 $\mu\text{g l}^{-1}$. It is clear that k_{pot} is related to the standing stock of phytoplankton in the water column, at least in waters where the standing stock is relatively low. This is intuitively reasonable since microbial abundance and activity are known to

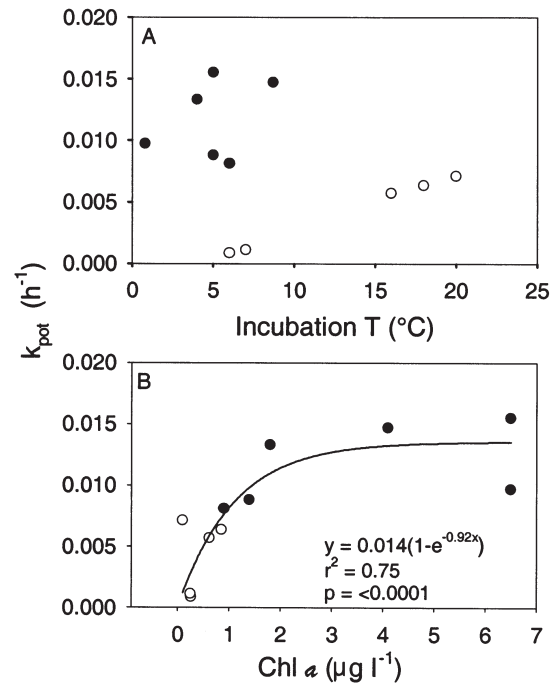


Fig. 8. Pooled potential rate constants (k_{pot}) from this study (o) and from Schultes et al. (2000) (●). (A) Plot of (k_{pot}) versus incubation temperature, showing no significant relationship; (B) relationship between k_{pot} and chlorophyll *a* concentration

be correlated with phytoplankton standing stock (Bird & Kalff 1984, Cole et al. 1988). The relationship between k_{pot} and chl *a* might be further bolstered if algal DMSP-lyases contribute significantly to the total lyase activity in seawater. Non-linear (inverse exponential) regression of the pooled data set shows a significant relationship ($r^2 = 0.75$, $p < 0.0001$) between k_{pot} and chl *a*. The plateau at higher chl *a* concentrations indicates that k_{pot} reaches a maximum in spite of increasing phytoplankton standing stock. This may be dependent on the species composition of the phytoplankton blooms in this region. However, this does not diminish the utility of the relationship in predicting k_{pot} based on chl *a*. Since chl *a* is easily measured remotely on synoptic scales, this finding could be of significant importance to efforts to model oceanic DMS production. The empirical prediction of rate constants from basic oceanographic variables would simplify the development of such models if the relationship shown here proves to be robust across a wider geographic and seasonal range.

Conclusions

Results from short-term kinetic incubations at 5 stations located in different areas of the North Atlantic

show that the potential community DMS production in the open ocean is a linear function of DMSP_d concentration and that it does not saturate, even at DMSP_d concentrations as high as 3000 nM. Longer-term experiments indicate that DMSP_d consumption rates were dependent on the concentration of DMSP_d, declining as the concentration declined. DMS production rates remained very constant as long as the dissolved DMSP substrate was present in sufficient quantities. Thus, the potential microbial DMS production following a phytoplankton bloom seems to be limited by the quantity of DMSP_d released, not by the inherent capacity of the microbial community to metabolize DMSP. The net conversion yield of 30 to 60% indicates that cleavage was very significant compared to demethylation and other processes, but the continuation of DMSP_d consumption after DMS production stopped suggests that demethylation and other processes dominate over DMSP cleavage at low DMSP_d concentrations. DMS consumption was insignificant across much of the study area, although high consumption rates observed in a *Chrysochromulina* sp. bloom suggest that DMS consumption may be enhanced in areas where ambient DMS concentrations are high. While correlation between the potential rate constant (k_{pot}) and water temperature was ambiguous, a significant non-linear relationship was found between k_{pot} and chl *a* standing stock when the data from this study were pooled with those of Schultes et al. (2000) from the Labrador Sea. These findings are potentially useful for predictive modelling of oceanic DMS production.

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