

## Biological consumption of dimethylsulfide (DMS) and its importance in DMS dynamics in the Ross Sea, Antarctica

Daniela A. del Valle,<sup>a</sup> David J. Kieber,<sup>b</sup> Dierdre A. Toole,<sup>c</sup> Jordan Brinkley,<sup>b</sup> and Ronald P. Kiene<sup>a,\*</sup>

<sup>a</sup>Department of Marine Sciences, University of South Alabama, Mobile, Alabama, and Dauphin Island Sea Lab, Dauphin Island, Alabama

<sup>b</sup>Department of Chemistry, State University of New York, College of Environmental Science and Forestry, Syracuse, New York

<sup>c</sup>Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

### Abstract

We studied the biological consumption of dimethylsulfide (DMS) and its role in controlling DMS concentrations in the Ross Sea, Antarctica, during the spring (Nov) and summer (Jan) of 2005. Surface DMS concentrations, measured with a technique that minimized DMS release from *Phaeocystis antarctica*, increased rapidly in the spring from 0.3 nmol L<sup>-1</sup> to 67.7 nmol L<sup>-1</sup>, paralleling increases in chlorophyll *a* and bacterial biomass production. Biological DMS consumption (BDMSC) rates were low (0.02 nmol L<sup>-1</sup> d<sup>-1</sup>) at the start of the bloom, but increased to 8.8 nmol L<sup>-1</sup> d<sup>-1</sup> at the peak of the bloom. Rate constants for BDMSC ( $k_{bc}$ ) remained relatively low throughout the spring (0.05–0.21 d<sup>-1</sup>) and this slow biological turnover contributed to the buildup of DMS during the early bloom. DMS concentrations in the summer (3.2–16.8 nmol L<sup>-1</sup>) were much lower than peak springtime concentrations, partly due to the higher BDMSC rate constants (0.22–0.98 d<sup>-1</sup>; i.e., faster biological turnover) in the summer. Kinetic analysis suggested that BDMSC rates were nearly saturated at ambient DMS concentrations in the spring but not in summer. BDMSC was mostly carried out in the size fractions <1 μm and >8 μm, except in the early spring when the <1-μm fraction (likely free-living bacteria) dominated BDMSC. BDMSC was the main removal pathway for DMS in the surface mixed layer during both the spring and summer, except during the prebloom, when photolysis dominated. BDMSC exerts a major control on DMS concentrations in the Ross Sea throughout the *Phaeocystis antarctica* bloom.

Dimethylsulfide (DMS) is a biogenic trace gas that is produced in the surface ocean from the degradation of the phytoplankton-metabolite dimethylsulfoniopropionate (DMSP). Sea–air transfer of DMS is estimated to contribute 0.5–1.0 Tmol of DMS per year to the global atmosphere (Kettle and Andreae 2000). Once in the atmosphere, DMS is oxidized to acidic aerosol particles, thereby affecting the Earth's radiative balance both directly, through the backscatter of solar radiation, and indirectly, through formation of cloud condensation nuclei (Charlson et al. 1987). The sea–air flux of DMS is directly proportional to the concentration of DMS in surface waters which, in turn, is controlled by a complex web of production and loss processes (Simó 2001). Enzymatically mediated production of DMS from DMSP can be carried out by both bacteria and phytoplankton (Stefels and Van Boekel 1993; Steinke et al. 1996). Once DMS is produced in surface waters, three mechanisms are primarily responsible for its removal: sea–air flux, photolysis, and biological DMS consumption (BDMSC; Bates et al. 1994). The relative importance of these three loss processes varies both spatially and temporally at mid- to low latitudes (Simó and Pedrós-Alió 1999; Vila-Costa et al. 2008). Relatively little is currently known about DMS cycling in high-latitude polar waters.

Some of the highest DMS concentrations in seawater worldwide (>300 nmol L<sup>-1</sup>) have been reported in the Ross Sea, Antarctica, associated with seasonal blooms of the phytoplankton *Phaeocystis antarctica* (DiTullio et al.

2003; Gambaro et al. 2004), a high-DMSP producer (Liss et al. 1994). The Ross Sea *P. antarctica* bloom typically begins in early to mid-November, with the timing and spatial distribution tied closely to loss of sea ice and the formation of the Ross Sea Polynya (Arrigo et al. 1998). DMS concentration data from the early bloom (Nov) are scarce (Gambaro et al. 2004), but high DMS concentrations have been reported for late December when the *P. antarctica* bloom typically peaks (DiTullio et al. 2003), while concentrations decrease by January as the bloom senesces (DiTullio et al. 2003). This seasonal DMS accumulation may be caused by a combination of factors including high DMS production rates, limitation of bacterial DMS consumption at low temperatures, and saturation of BDMSC rates (Wolfe et al. 1999; DiTullio et al. 2003). Microbial consumption of DMS has been shown to saturate at ~10–30 nmol L<sup>-1</sup> DMS (Wolfe and Kiene 1993a; Wolfe et al. 1999); hence, unusual accumulation episodes of DMS in the Ross Sea may be facilitated by a limited ability of microbes to consume it.

Consumption of DMS by microbes in temperate and subtropical waters can be responsible for turning over the standing DMS pool in <1 d, although typical turnover times are 1–4 d (Kiene and Bates 1990; Bates et al. 1994; Toole et al. 2006). Simó (2004) compiled results from different studies done in temperate and subtropical waters and concluded that BDMSC can remove 50–80% of the DMS produced in seawater. Likewise, an observational and modeling study of the Barents Sea found that BDMSC was generally more important than photolysis and ventilation as a removal mechanism for DMS during a phytoplankton bloom (Gabric et al. 1999).

\* Corresponding author: rkiene@disl.org

Initial estimates of BDMSC for the Ross Sea show that this process is potentially important in regulating DMS emissions to the atmosphere, with BDMSC turnover times of  $\sim 1$  d (DiTullio et al. 2003; Kiene et al. 2007). However, the magnitude and importance of BDMSC has not been investigated in detail in the Ross Sea or in any other area of the Southern Ocean. We, therefore, carried out a study of the seasonal and vertical distribution of BDMSC rates in the Ross Sea and evaluated its role in controlling DMS concentrations. In addition, we determined the kinetic response of BDMSC to DMS concentrations and identified the size fractions of the biological community responsible for DMS consumption. Based on these results, we assessed the relative importance of BDMSC in the removal of DMS from the water column in this climatically important, yet understudied region.

## Methods

Seawater samples were collected in the spring (Nov 05) and summer (Dec 04–Jan 05) during two cruises to the Ross Sea, Antarctica, aboard the RVIB *Nathaniel B. Palmer*. During each cruise, several stations were occupied for 4–7 d each (Fig. 1) and surface seawater samples (0–10 m) were collected daily. In addition to the daily surface samples, two depth profiles (6–7 depths) were obtained at each station to determine BDMSC rate constants and DMS concentrations. All seawater samples were collected with 20-liter Niskin bottles attached to a conductivity, temperature, and depth (CTD) rosette. CTD casts were carried out in the morning (06:00–08:00 h, local New Zealand time), except on 25 November 2005, when the cast was at 16:30 h, local time. Ancillary data such as chlorophyll *a* (Chl *a*) concentrations and leucine incorporation rates were also collected. The mixed-layer depth was determined from CTD profiles, and was defined as the depth at which  $\sigma_t$  increased by  $0.01 \text{ kg m}^{-3}$  from the average near-surface (1–3 m) value.

Biological processes consume DMS and transform it into nonvolatile forms including sulfate, DMSO, cellular material, and other unidentified dissolved sulfur species (Kiene and Linn 2000; del Valle et al. 2007). The BDMSC rate constant ( $k_{bc}$ ) was obtained by quantifying the conversion of tracer levels of radiolabeled  $^{35}\text{S}$ -DMS into nonvolatile products in dark incubations (Kiene and Linn 2000). The method used here is described in detail in del Valle et al. (2007). Briefly, water samples were transferred from Niskin bottles into acid-cleaned polycarbonate bottles using silicone tubing. Seawater from each depth was carefully poured from the polycarbonate bottles into duplicate muffled (2 h,  $450^\circ\text{C}$ ) 7-mL serum vials, leaving no more than 10% of the vial volume as headspace. Vials were sealed with Teflon-faced butyl rubber stoppers and each was amended via syringe with gaseous  $^{35}\text{S}$ -DMS at nonperturbing concentrations ( $1000\text{--}3000 \text{ dpm mL}^{-1}$ ;  $<1 \text{ pmol L}^{-1}$ ). Radiolabeled DMS was obtained from  $^{35}\text{S}$ -DMSP by alkaline cleavage (specific activity =  $0.3 - 2 \times 10^6 \text{ dpm pmol}^{-1}$ ). Tracer-amended samples were incubated in the dark in a water bath filled with flowing surface seawater. Single-time point samples were collected after 4–

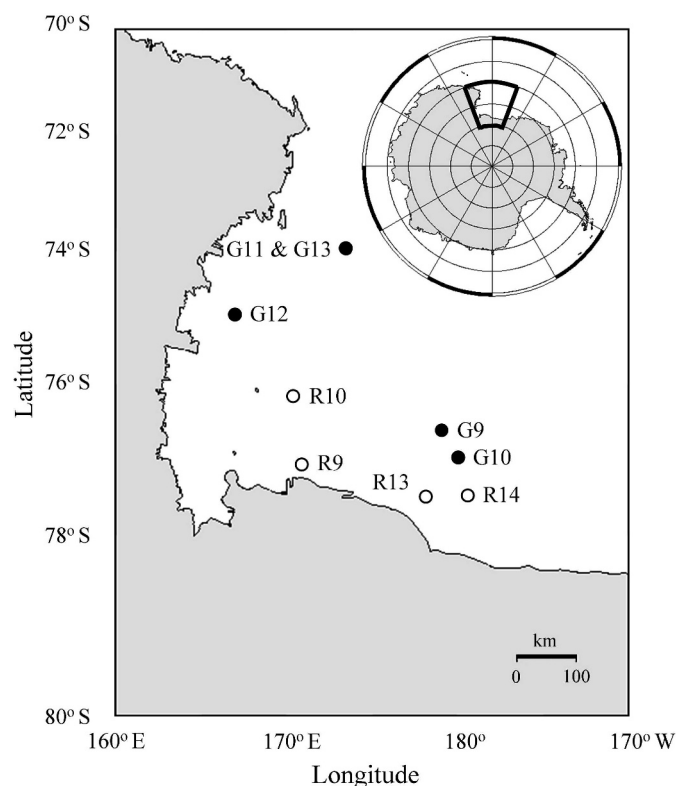


Fig. 1. Geographic location of stations sampled during two cruises to the Ross Sea, one in the spring and one in the summer of 2005: R9 (09 Nov 05), R10 (10–14 Nov 05), R13 (18–23 Nov 05), R14 (25–30 Nov 05), G9 (28–29 Dec 04), G10 (30 Dec 04–02 Jan 05), G11 (03–08 Jan 05), G12 (09–15 Jan 05), and G13 (16–21 Jan 05).

8-h incubations, depending on the sampling date. At the end of the incubation, the total radioactivity added to each vial ( $A_{\text{total}}$ ) was determined by counting a 1-mL subsample of the water in Ecolume scintillation fluid. Samples were then sparged with  $\text{N}_2$  for 10 min to remove any untransformed  $^{35}\text{S}$ -DMS. The remaining nonvolatile  $^{35}\text{S}$  products ( $A_{\text{NV}}$ ) were quantified by pipetting 1-mL subsamples of the sparged sample into Ecolume. The fraction of added  $^{35}\text{S}$ -DMS transformed into nonvolatile products was calculated as  $A_{\text{NV}} / A_{\text{total}}$  and, therefore, the fraction of  $^{35}\text{S}$ -DMS remaining was equal to  $1 - (A_{\text{NV}} / A_{\text{total}})$ . The value of  $k_{bc}$  is the slope of the natural log of the fraction of untransformed  $^{35}\text{S}$ -DMS (i.e.,  $\ln [1 - A_{\text{NV}} / A_{\text{total}}]$ ) vs. time. This calculation assumes first-order loss kinetics for the added tracer (Kiene and Linn 2000) and steady-state DMS concentrations. The BDMSC rate was calculated by multiplying the  $k_{bc}$  by the corresponding DMS concentration. Periodic tests showed that unlabeled DMS concentrations did not change appreciably during our incubations, supporting our steady-state assumption for DMS concentrations.

DMS concentrations were determined using a purge-and-trap system followed by gas chromatography with flame photometric detection (Kiene and Service 1991). To minimize DMS release from plankton, sample processing protocols were modified slightly from those used previous-

ly. Unless otherwise noted, seawater samples were gently prescreened through 20- $\mu\text{m}$  Nitex mesh either by holding the mesh in the mouth of the sample collection bottle and allowing water from the Niskin bottle to flow tangentially over and through the mesh, or by filtering the sample through a 47-mm magnetic filter holder containing the Nitex mesh as the filter. With either procedure, the Nitex mesh removed larger particles (e.g., *P. antarctica* colonies) with minimal physical disturbance. The screened water was collected into 30–60-mL Teflon bottles with no headspace and placed in a dark water bath at the in situ temperature until analysis (<1 h). A 2–4-mL aliquot of the prescreened seawater was subsequently taken up in an all-glass syringe and injected through a 25-mm-diameter Whatman GF/F glass-fiber filter directly into a 14-mL serum vial that was sealed with a Teflon-faced butyl rubber stopper. The sealed vial was connected to the purge-and-trap system by way of a syringe needle and Teflon tubing. This prescreening method was selected based on preliminary tests carried out during the summer cruise when diatoms and single-celled *P. antarctica* dominated the phytoplankton assemblage. A systematic evaluation of several sample-processing procedures was carried out during the November 2005 cruise when the phytoplankton community was dominated by colonial *P. antarctica*. For several dates on this cruise, seawater samples were either (1) screened through a 20- $\mu\text{m}$  Nitex mesh and then syringe-filtered through a Whatman GF/F filter (20  $\mu\text{m}$  + GF/F); (2) collected unfiltered in a 30-mL Teflon bottle and syringe-filtered through a Whatman GF/F filter (GF/F only); or (3) left unfiltered before introduction into the purge-and-trap system. Triplicate or quadruplicate samples were analyzed for each treatment. All samples were sparged with He for 5 min at 100 mL  $\text{min}^{-1}$  to cryotrap DMS before injection into the chromatographic system. Samples processed with the different treatments were analyzed in random order to minimize storage bias, because analysis of all the samples required up to 1 h to complete. On one occasion, DMS concentrations obtained using the 20  $\mu\text{m}$  + GF/F method were compared to DMS concentrations obtained using Slide-a-Lyzer dialysis cassettes (with a 10,000 molecular weight cutoff; Pierce Chemical). Dialysis cassettes were submerged in a 100-liter open bucket filled with surface water. Cassettes were left to attain equilibrium for 2 h and then removed for DMS analysis; a separate study with Antarctic waters showed that equilibrium for dissolved solutes was achieved in 2 h (Kiene and Slezak 2006). At the same time that cassettes were removed, DMS samples were also collected from the bucket using the 20  $\mu\text{m}$  + GF/F method.

For Chl *a* analysis, plankton were concentrated onto 25-mm-diameter Gelman AE glass-fiber filters, which were subsequently extracted with 90% acetone for 24 h at  $-20^{\circ}\text{C}$ . The Chl *a* concentration in the extracts was determined fluorometrically using the acidification method (Strickland and Parsons 1972). Leucine incorporation rates, used as an index of bacterial protein synthesis, were measured using the  $^3\text{H}$ -leucine incorporation method, as modified for small sample sizes (Smith and Azam 1992). For each sample, 20 nmol  $\text{L}^{-1}$   $^3\text{H}$ -leucine was added to four replicate seawater subsamples (1.5 mL each) in 2-mL

microcentrifuge tubes. Prior to addition of  $^3\text{H}$ -leucine, one of the replicates was treated with trichloroacetic acid (TCA; 5% final concentration) to serve as a killed control. Single-time point incubations, lasting 1 h (Jan 05) or 1–5 h (Nov 05), were conducted in the dark at surface seawater temperature.

*DMS sea-air flux and photolysis*—The DMS flux from seawater to the atmosphere was calculated from the wind speed, surface seawater temperature, and DMS concentration using the method outlined in Nightingale et al. (2000). Wind-speed data, collected from an anemometer placed at 37 m above sea level on the ship's mast, were corrected to 10-m height using the logarithm profile method (Roll 1965) and averaged hourly before applying the parameterization to obtain the transfer velocity.

Depth-dependent DMS photolysis rates were determined by multiplying depth-dependent photolysis rate constants by water-column DMS concentrations. First-order photolysis rate constants ( $k_p$ ) were calculated according to Bailey et al. (2008). Briefly,  $k_p$  was computed as a function of depth by integrating the wavelength-dependent (290–600 nm) product of the absorption of chromophoric dissolved organic matter (aCDOM), the scalar light flux ( $E_o$ ), and the apparent quantum yield (AQY) for the photochemical loss of DMS. Depth-dependent aCDOM and  $E_o$  spectra were measured throughout the upper water column as described in Kieber et al. (2007) and Bailey et al. (2008), respectively.

The wavelength dependence of the AQY for DMS photolysis in the Ross Sea water samples was determined according to the polychromatic irradiation method outlined in Bailey et al. (2008). Surface seawater samples were gravity-filtered first through a 47-mm magnetic filter holder containing 20- $\mu\text{m}$  Nitex mesh followed by a 0.2- $\mu\text{m}$  nylon cartridge filter (Toole et al. 2003) to remove all organisms. This filtration procedure did not appreciably change the natural DMS concentration. Filtered samples were transferred to quartz tubes and subsequently amended with tracer levels of  $^{35}\text{S}$ -DMS. Quartz tubes were incubated on the deck of the ship in a shallow polychromatic incubator with eight spectral treatments (Bailey et al. 2008). The temperature in the incubator was controlled by flowing surface seawater. The light dose under each spectral treatment was determined with nitrite chemical actinometry (Kieber et al. 2007). Duplicate quartz tubes and actinometers were set out for each spectral treatment in addition to several aluminum foil-wrapped, dark controls. Samples were exposed to solar radiation for 1–6 h, depending on the spectral treatment. After exposure to solar radiation, photolysis samples and dark controls were processed identically to those described above for BDMSC to determine the fraction of added tracer converted to nonvolatile  $^{35}\text{S}$ . Actinometry and DMS photolysis data were then used to calculate AQY according to Bailey et al. (2008).

*Size-fractionated BDMSC rate constants*—BDMSC rate constants were measured in unfiltered water as well as in seawater filtered through either a 1-, 3-, or 8- $\mu\text{m}$  Nuclepore polycarbonate filter held in an acid-rinsed, 47-mm-diameter

Table 1. DMS concentrations obtained by helium sparging of seawater that was either passed through a 20- $\mu\text{m}$  mesh followed by filtration through a GF/F filter (20  $\mu\text{m}$  + GF/F), filtered through a GF/F filter only (GF/F only), left unfiltered (Unfiltered), or collected using Slide-A-Lyzers (SAL) dialysis cassettes. All samples were from the Ross Sea, Antarctica, and contained colonial *P. antarctica* as the dominant phytoplankter. DMS concentrations are the mean of three or four replicates  $\pm$  standard deviation.

Date	Sampling depth (m)	DMS (nmol L <sup>-1</sup> )			
		20 $\mu\text{m}$ +GF/F	GF/F only	Unfiltered	SAL
23 Nov 05*	5	41.4 $\pm$ 0.4	62.3 $\pm$ 2.5	No data	No data
24 Nov 05†	20	40.6 $\pm$ 2.0	86.8 $\pm$ 14.7	249.5 $\pm$ 24.8	No data
24 Nov 05‡	1	30.1 $\pm$ 0.3	No data	No data	29.0 $\pm$ 0.9
25 Nov 05*	10	No data	83.2 $\pm$ 4.9	219.6 $\pm$ 13.2	No data
25 Nov 05†	5	44.7 $\pm$ 2.2	84.7 $\pm$ 5.1	198.9 $\pm$ 13.9	No data
28 Nov 05†	5	63.2 $\pm$ 1.9	72.3 $\pm$ 7.2	236.0 $\pm$ 25.9	No data

\*  $p < 0.05$ ,  $t$ -test,  $n_1 = n_2 = 4$ ,  $df = 6$ .

†  $p < 0.05$ , one-way ANOVA,  $p < 0.05$  among all pairs; Tukey's test.

‡  $p = 0.33$ , Mann-Whitney Rank Sum Test,  $n$  (small) =  $n$  (big) = 3.

polycarbonate filter holder. The filter holder was connected directly to the Niskin bottle with silicone tubing and hydrostatic pressure forced water through the filter. A piece of 20- $\mu\text{m}$  Nitex mesh was placed in-line before the Nuclepore filter to remove larger particles. Additional size fractions were obtained by passing seawater directly through 20- $\mu\text{m}$  or 100- $\mu\text{m}$  Nitex mesh. Each size fraction was run in triplicate. All filtrate samples were collected in 60-mL Teflon bottles and then carefully transferred into muffled glass serum bottles in order to determine BDMSC rate constants. The DMS concentration in each fraction was determined immediately after filtration to verify that the natural DMS concentration of the sample was not substantially affected by the filtration; deviations from DMS concentrations in 20- $\mu\text{m}$ -mesh-filtered seawater samples were <10%.

**Kinetic parameters**—For determination of BDMSC kinetic parameters, unfiltered seawater from 5 m was partitioned into a series of 250-mL Teflon bottles, leaving no headspace. Bottles were amended with unlabeled DMS and left in the dark for half an hour at the in situ temperature to ensure homogenization of the added DMS. For each experiment, bottles with six to nine different DMS concentrations were prepared, ranging from at or below the in situ concentration up to  $\sim 150$  nmol L<sup>-1</sup>. Three kinetic experiments were carried out during the summer and two were conducted during the spring. In the spring experiments, two treatments with DMS concentrations lower than the in situ concentration were obtained by allowing sample bottles to sit uncovered for half an hour at the in situ temperature. DMS concentrations were measured in each bottle and then subsamples from each were amended with <sup>35</sup>S-DMS for BDMSC rate-constant determinations. Subsamples were incubated in the dark for 3.5 h and processed for production of nonvolatile <sup>35</sup>S as previously described. BDMSC rates were calculated by multiplying the BDMSC rate constant by the DMS concentration in each incubation bottle. The Michaelis-Menten parameters,  $K_s$  (half-saturation constant) and  $V_m$  (saturation consumption rate), were obtained using nonlinear regression analysis. In this study, kinetic parameters describe the activity of whole

cells of a natural planktonic assemblage, rather than the activity of a single enzyme or species.

## Results

**DMS concentrations**—DMS concentrations measured by sparging unfiltered water samples were significantly higher than those obtained by sparging filtered (GF/F only) or screened and then filtered (20  $\mu\text{m}$  + GF/F) samples (Table 1). We also found that syringe filtering directly through a GF/F filter yielded higher DMS concentrations than when the sample was first passed through a 20  $\mu\text{m}$  screen to remove large *P. antarctica* colonies prior to GF/F filtration (Table 1). Additional tests (not shown) revealed that DMS was released from non-screened water samples during the syringe-filtration and sparging steps, presumably due to physical effects on *P. antarctica* cells or colonies. Furthermore, concentrations obtained from prescreened samples had lower variability (1–5% relative standard deviation [RSD]) compared to GF/F-filtered and unfiltered samples (4–17% and 6–11% RSD, respectively). In a separate experiment, DMS concentrations obtained using the 20  $\mu\text{m}$  + GF/F approach were not significantly different from DMS concentrations obtained from dialysis samplers (Table 1). Collectively, these results show that sparging GF/F-filtered or unfiltered samples without pre-screening can result in a two-fold (for GF/F-filtered samples) or up to a six-fold (for unfiltered samples) overestimation of DMS concentrations in samples containing *P. antarctica*. Based on these results, we chose to pre-screen all samples collected for DMS concentration determination during this study.

**Seasonal variation**—We initially sampled the Ross Sea during the summer (Dec 04 and Jan 05) and then returned the following spring (Nov 05). Because bloom cycles are relatively predictable in the Ross Sea, we present data in a logical spring–summer sequence, with the caveat that our data are not from one continuous season.

**Spring:** Upon our arrival in the Ross Sea in the early spring (09 Nov 05), the polynya had not yet fully opened, and only small amounts of open water were present.

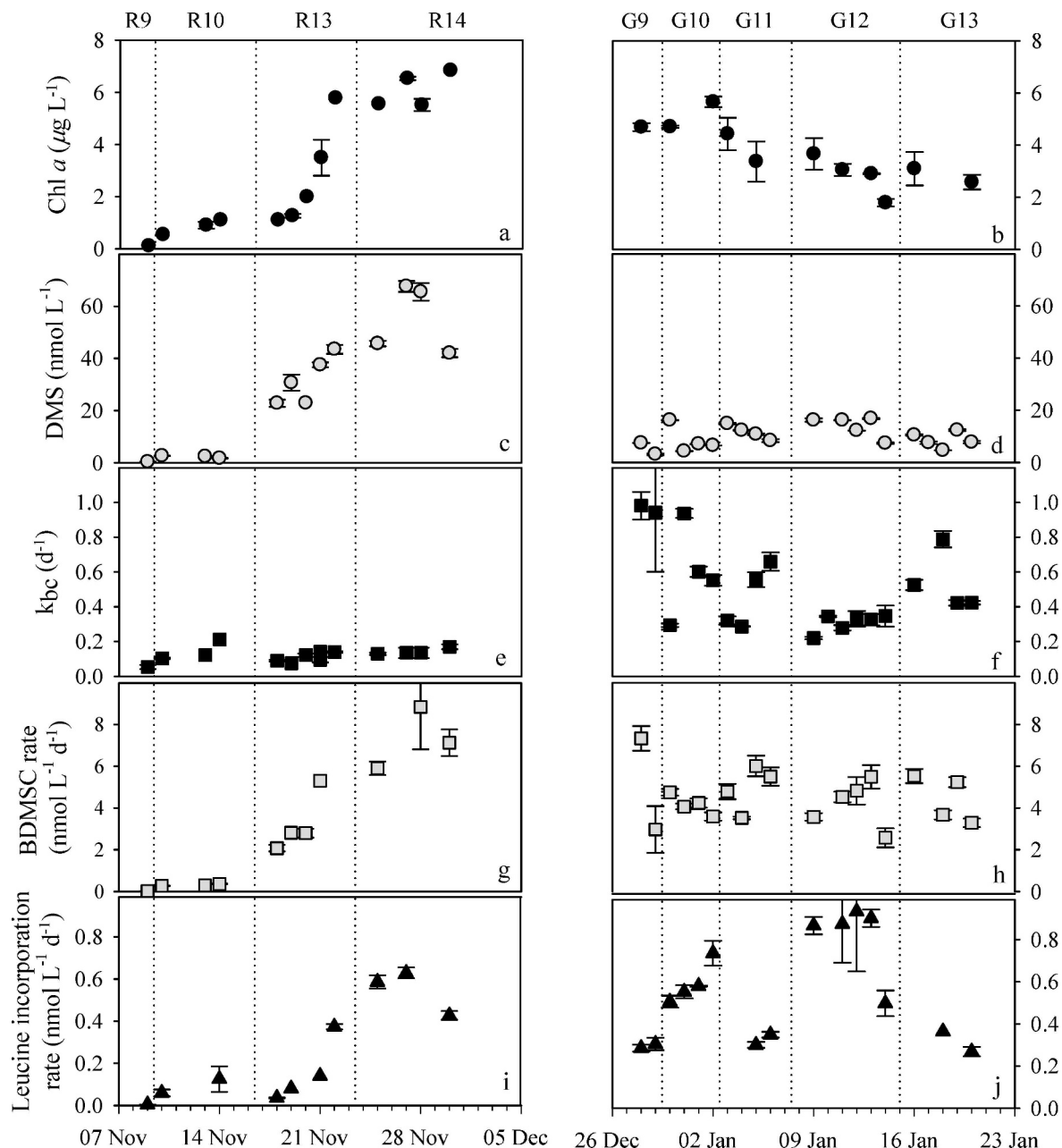


Fig. 2. Near-surface (0–10 m) values of (a, b) Chl *a*, (c, d) DMS concentration, (e, f)  $k_{bc}$ , (g, h) BDMSC rate, and (i, j) leucine incorporation rate during the spring and summer in the Ross Sea. Vertical dotted lines denote a change in sampling location within the Ross Sea. Vertical error bars denote the range of duplicate measurements and are shown when bigger than symbols. Panels on the left correspond to the spring (Nov 05) and panels on the right correspond to the previous summer (Jan 05).

Surface Chl *a* concentrations remained low ( $<1.1 \mu\text{g L}^{-1}$ ) until 20 November when Chl *a* started to increase rapidly due to a bloom of colonial *P. antarctica*, reaching a maximum value of  $6.8 \mu\text{g L}^{-1}$  on 30 November (Fig. 2a). Surface leucine incorporation rates (Fig. 2i), a measure of bacterial biomass production, increased concurrently with Chl *a* concentrations ( $r = 0.93$ ,  $p < 0.01$ ,  $n = 8$ ), suggesting an increase in the general bacterial activity associated with phytoplankton biomass. Surface DMS concentrations also increased rapidly, from  $0.3 \text{ nmol L}^{-1}$  in early November to values as high as  $67.7 \text{ nmol L}^{-1}$  by 28 November (Fig. 2c).

DMS concentrations were positively correlated with Chl *a* during this time ( $r = 0.82$ ,  $p = 0.007$ ,  $n = 9$ ). Despite the increase in DMS concentrations, biological DMS consumption (BDMSC) rate constants ( $k_{bc}$ ) in surface waters remained low and relatively constant throughout November (range =  $0.05$ – $0.21 \text{ d}^{-1}$ , mean =  $0.12 \text{ d}^{-1}$ ; Fig. 2e), and they were not correlated to changes in Chl *a* ( $p = 0.36$ ,  $n = 9$ ), DMS concentrations ( $p = 0.71$ ,  $n = 11$ ), or leucine incorporation rates ( $p = 0.23$ ,  $n = 12$ ). On the other hand, surface BDMSC rates did increase together with Chl *a* ( $r = 0.94$ ,  $p < 0.001$ ,  $n = 8$ ) and leucine incorporation rates ( $r =$

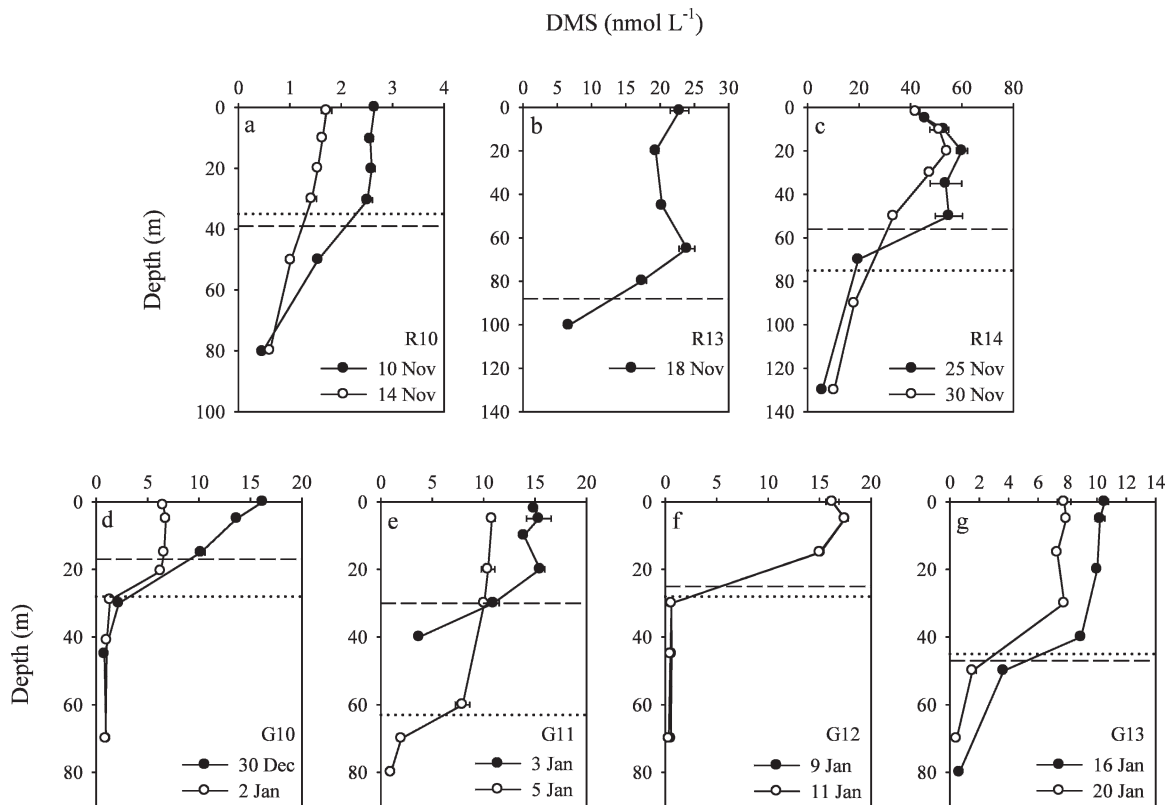


Fig. 3. Vertical profiles of DMS concentrations during the (a–c) spring and (d–g) summer. Dashed lines represent the depth of the ML corresponding to the solid-black circle profiles, while dotted lines represent the depth of the ML for the open-circle profiles. Horizontal error bars denote the range of duplicate measurements. Each panel shows profiles corresponding to a specific station. For station locations refer to Fig. 1. In panel f, the two profiles shown for Station G12 are nearly identical and the symbols overlay one another.

0.79,  $p = 0.02$ ,  $n = 8$ ), rising from 0.02  $\text{nmol L}^{-1} \text{d}^{-1}$  on 09 November to a maximum of 8.8  $\text{nmol L}^{-1} \text{d}^{-1}$  on 28 November (Fig. 2g).

Summer: Surface Chl *a* concentrations were relatively high (1.8–5.7  $\mu\text{g L}^{-1}$ ) during the summer and generally declined during the sampling period (28 Dec–21 Jan; Fig. 2b). The phytoplankton community was mostly composed of a mix of single-celled *P. antarctica* and several different small pennate diatoms, with *Pseudonitzschia subcurvata* being the most abundant species (D. Karentz pers. comm.). Surface-water DMS concentrations showed no temporal trend in the summer and were lower than during late November, with values ranging from 3.2  $\text{nmol L}^{-1}$  to 16.8  $\text{nmol L}^{-1}$  (Fig. 2d). Unlike the spring period, DMS concentrations in summer were not correlated with Chl *a* ( $p = 0.95$ ,  $n = 11$ ). Summertime surface  $k_{bc}$  values were considerably higher than during the spring, ranging from 0.22  $\text{d}^{-1}$  to 0.98  $\text{d}^{-1}$  (mean = 0.51  $\text{d}^{-1}$ ; Fig. 2f). During the summer season, surface  $k_{bc}$  values were not correlated to Chl *a* ( $p = 0.30$ ,  $n = 11$ ) but were negatively correlated to leucine incorporation rates ( $r = -0.62$ ,  $p = 0.012$ ,  $n = 15$ ) and DMS concentrations ( $r = -0.82$ ,  $p < 0.001$ ,  $n = 19$ ). Surface BDMSC rates ranged from 2.6  $\text{nmol L}^{-1} \text{d}^{-1}$  to 7.3  $\text{nmol L}^{-1} \text{d}^{-1}$ , with an average of 4.5  $\text{nmol L}^{-1} \text{d}^{-1}$  (Fig. 2h), and were not correlated to

Chl *a* ( $p = 0.36$ ,  $n = 11$ ) or leucine incorporation rates ( $p = 0.78$ ,  $n = 15$ ).

**Depth profiles**—Concentrations of DMS were generally uniform throughout the surface mixed layer (ML), and for any given profile, ML concentrations (1.4–60.0  $\text{nmol L}^{-1}$ , spring; 6.3–17.5  $\text{nmol L}^{-1}$ , summer) were higher than concentrations below the ML (0.5–19.7  $\text{nmol L}^{-1}$ , spring; 0.4–10.9  $\text{nmol L}^{-1}$ , summer; Fig. 3). During the spring,  $k_{bc}$  ranged from 0.09  $\text{d}^{-1}$  to 0.26  $\text{d}^{-1}$  within the ML and from 0.06  $\text{d}^{-1}$  to 1.26  $\text{d}^{-1}$  below it (Fig. 4a–c). There was relatively little vertical variation in  $k_{bc}$  in the spring, except on 30 November (the last spring date sampled) when values below the ML were on average 3.5-fold higher than in the ML. This distinctive pattern observed at the end of November was also observed throughout the summer (Fig. 4d–g), with 2–7-fold higher  $k_{bc}$  values below the mixed layer (0.56–6.17  $\text{d}^{-1}$ ) compared to mean values in the ML (0.20–0.88  $\text{d}^{-1}$ ).

Higher springtime BDMSC rates were observed in the ML (0.14–5.9  $\text{nmol L}^{-1} \text{d}^{-1}$ ) than below it (0.03–2.4  $\text{nmol L}^{-1} \text{d}^{-1}$ ; Fig. 5a–c), except for 30 November. Because BDMSC rates are calculated as the product of  $k_{bc}$  and the DMS concentration, and  $k_{bc}$  varied little with depth during this time period (Fig. 4a–c), the shape of the spring

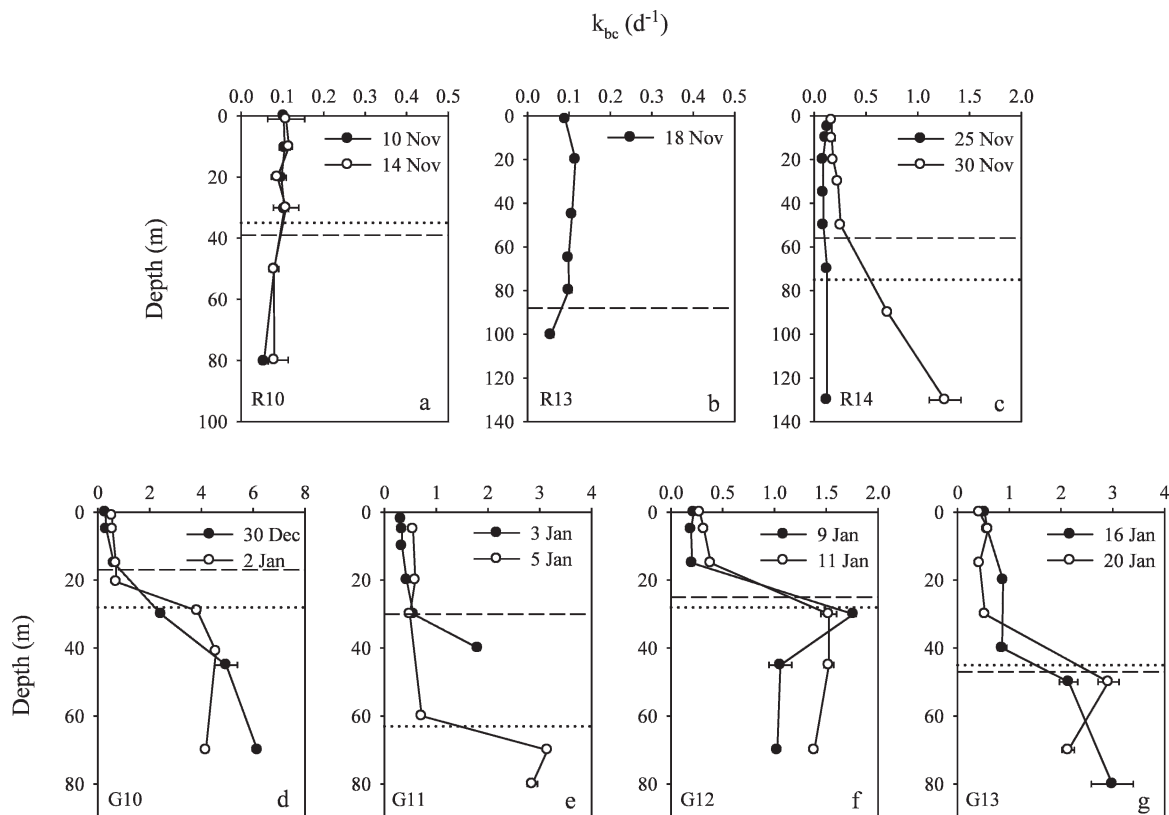


Fig. 4. Vertical profiles of biological DMS consumption rate constants ( $k_{bc}$ ) during the (a–c) spring and (d–g) summer. Dashed lines represent the depth of the ML corresponding to the solid-black circle profiles, while dotted lines represent the depth of the ML for the open-circle profiles. Horizontal error bars denote the range from duplicate measurements. Each panel shows profiles corresponding to a specific station. For station locations refer to Fig. 1.

BDMSC rate profiles (Fig. 5a–c) was mostly determined by the DMS concentration profiles (Fig. 3a–c). During the summer, DMS concentrations and  $k_{bc}$  followed opposite patterns (Figs. 3 and 4d–g). Thus, BDMSC rates did not have vertical distributions as pronounced as those for  $k_{bc}$  or DMS concentration (Fig. 5d–g), with the exception of 09 January and 11 January (Sta. G12), when the average ML BDMSC rates were 3.2- and 5.7-fold higher than rates below the ML. Summertime BDMSC rates ranged from 3.1  $\text{nmol L}^{-1} \text{d}^{-1}$  to 8.8  $\text{nmol L}^{-1} \text{d}^{-1}$  in the mixed layer, and from 0.5  $\text{nmol L}^{-1} \text{d}^{-1}$  to 7.8  $\text{nmol L}^{-1} \text{d}^{-1}$  at deeper depths.

**Kinetic parameters**—Kinetic parameters for BDMSC in the mixed layer were obtained from five experiments spanning the spring and summer (Table 2). A typical kinetic response of BDMSC rates to different DMS concentrations is shown in Fig. 6. The half-saturation constants ( $K_s$ ) for BDMSC on the two spring dates (20 and 27 Nov) were 10.6  $\text{nmol L}^{-1}$  and 15.3  $\text{nmol L}^{-1}$ , respectively, and these  $K_s$  values were two- and four-fold lower than corresponding in situ DMS concentrations. In contrast, summertime  $K_s$  values (7.9–21.5  $\text{nmol L}^{-1}$ ) were 1.1–5.0 times higher than corresponding in situ DMS concentrations. Saturation consumption rates ( $V_m$ ) ranged from 4.0  $\text{nmol L}^{-1} \text{d}^{-1}$  to 11.7  $\text{nmol L}^{-1} \text{d}^{-1}$  in the spring

and from 8.9  $\text{nmol L}^{-1} \text{d}^{-1}$  to 28.8  $\text{nmol L}^{-1} \text{d}^{-1}$  in the summer (Table 2).

**Size fractionation**—BDMSC rate constants were determined on five different dates (10 Nov, 30 Nov, 05 Jan, 09 Jan, 16 Jan 05) in both whole seawater ( $k_{bc}$ ) and 1- $\mu\text{m}$ -filtered seawater ( $k_{1\mu\text{m}}$ ) in order to assess the relative contribution of free-living bacteria (<1  $\mu\text{m}$ ) to BDMSC compared to the whole biological community (i.e., free-living and attached bacteria, and phytoplankton). Free-living bacteria (<1  $\mu\text{m}$ ) contributed nearly all of the observed BDMSC in the early spring before the onset of the bloom (water column average for  $k_{1\mu\text{m}}$  was 95% of  $k_{bc}$ ; Fig. 7). Free-living bacteria were less important during late November and summer, with  $k_{1\mu\text{m}}$  accounting for 36–73% of the total  $k_{bc}$ , respectively. No obvious pattern was observed in the relative contribution of the <1- $\mu\text{m}$  size fraction to  $k_{bc}$  with respect to station location or sample depth (Fig. 7).

During the summer, two detailed size-fractionation experiments were carried out with seawater collected from 5 m. On 31 December 2004, BDMSC rate constants in the <1- $\mu\text{m}$ , <3- $\mu\text{m}$ , <8- $\mu\text{m}$ , <20- $\mu\text{m}$ , and <100- $\mu\text{m}$  size fractions were 62 ( $\pm 3$ ), 69 ( $\pm 4$ ), 68 ( $\pm 3$ ), 79 ( $\pm 5$ ), and 94 ( $\pm 5$ ) %, respectively, of the BDMSC rate constant measured in unfiltered seawater, while on 12 January

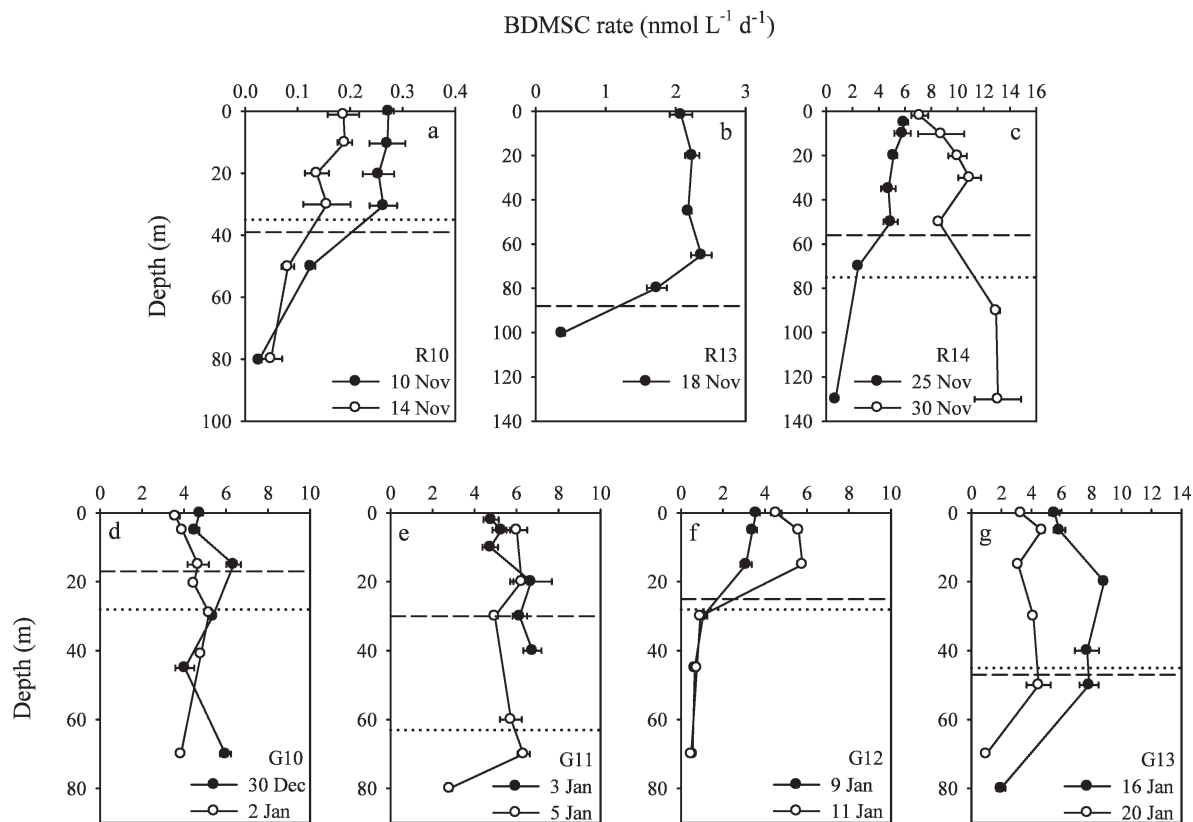


Fig. 5. Vertical profiles of biological DMS consumption (BDMSC) rates during the (a–c) spring and (d–g) summer. Dashed lines represent the depth of the mixed layer corresponding to the solid-black circle profiles, while dotted lines represent the depth of the ML for the open-circle profiles. Horizontal bars denote the range from duplicate measurements. Each panel shows profiles corresponding to a specific station. For station locations refer to Fig. 1.

2005 rate constants in these same size fractions were  $52 (\pm 5)$ ,  $50 (\pm 6)$ ,  $52 (\pm 4)$ ,  $72 (\pm 7)$ , and  $94 (\pm 9)$  % of the value in unfiltered seawater. In both experiments, no significant difference in BDMSC rate constants was observed between the free-living bacteria fraction ( $<1 \mu\text{m}$ ) and the  $<3\text{-}\mu\text{m}$  or

the  $<8\text{-}\mu\text{m}$  fractions ( $p < 0.05$ , one-way ANOVA, Tukey's test), suggesting that microbes in particles between  $1 \mu\text{m}$  and  $8 \mu\text{m}$  did not contribute significantly to BDMSC. BDMSC rate constants in the  $<20\text{-}\mu\text{m}$  and  $<100\text{-}\mu\text{m}$  size fractions were significantly different from the rate constants in the  $<8\text{-}\mu\text{m}$  fraction ( $p < 0.05$ , one-way ANOVA, Tukey's test), with particles between  $8 \mu\text{m}$  and  $100 \mu\text{m}$  contributing from 26% to 42% of the total observed BDMSC. Particles larger than  $100 \mu\text{m}$  did not contribute to BDMC because no significant difference was observed in either experiment between the  $<100\text{-}\mu\text{m}$  size fraction and unfiltered seawater.

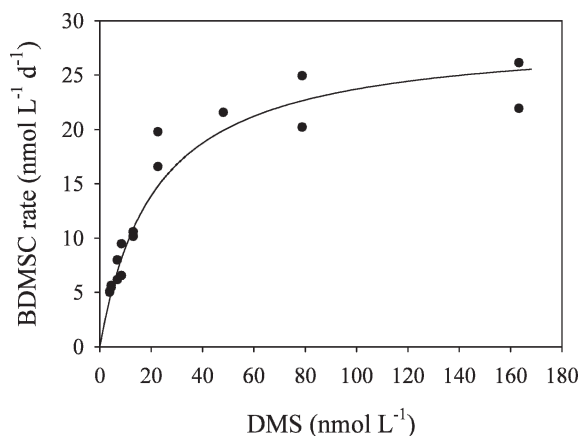


Fig. 6. Kinetic curve for BDMSC in unfiltered seawater collected on 18 January 2005. Concentrations above ambient ( $4.9 \text{ nmol L}^{-1}$ ) were obtained by experimental additions of gaseous DMS. The black line depicts the fit to the data to the Michaelis–Menten equation obtained using nonlinear regression analysis:  $\text{rate} = 28.9[\text{DMS}] / (21.5 + [\text{DMS}])$ ,  $r^2 = 0.94$ .

*Comparison of DMS loss processes*—Mixed-layer-integrated losses of DMS due to the sum of BDMSC, photolysis, and sea–air flux ranged from  $55 \mu\text{mol m}^{-2} \text{ d}^{-1}$  to  $1049 \mu\text{mol m}^{-2} \text{ d}^{-1}$  in the spring, and from  $143 \mu\text{mol m}^{-2} \text{ d}^{-1}$  to  $610 \mu\text{mol m}^{-2} \text{ d}^{-1}$  in the summer (Fig. 8). By comparison, the loss of DMS from the ML by downward vertical mixing was negligible ( $<4.5 \mu\text{mol m}^{-2} \text{ d}^{-1}$ ;  $<1.2\%$  of total losses) and will not be considered further. Turnover times (i.e.,  $1/\text{loss rate constant}$ ) for the pool of DMS in the ML due to the sum of BDMSC, photolysis, and sea–air flux ranged from 3.2 d to 7.9 d in the spring and from 0.8 d to 2.3 d in the summer. BDMSC was the dominant loss process for ML DMS once the bloom started to develop, accounting for 59.8% to 89.2%

Table 2. Kinetic parameters ( $K_s$  [half-saturation constant] and  $V_m$  [max. consumption rate]) for biological DMS consumption (BDMSC) in seawater from the Ross Sea, Antarctica. Kinetic parameters were calculated using nonlinear regression analysis of rate vs. concentration data in experiments similar to that shown in Fig. 6. Also shown are the in situ DMS concentrations and the BDMSC rates on each of the sampling dates. All samples were collected from 5 m.

Date	$K_s \pm SE$ ( $\text{nmol L}^{-1}$ )*	$V_m \pm SE$ ( $\text{nmol L}^{-1} \text{d}^{-1}$ )*	$r^2$	In situ DMS concentration ( $\text{nmol L}^{-1}$ )	In situ BDMSC rate ( $\text{nmol L}^{-1} \text{d}^{-1}$ )
20 Nov 05	$10.6 \pm 3.8$	$4.0 \pm 0.3$	0.90	22.9	2.8
27 Nov 05	$15.3 \pm 8.8$	$11.7 \pm 1.9$	0.80	65.3	8.4
31 Dec 04	$12.0 \pm 1.6$	$11.3 \pm 0.5$	0.91	4.3	3.1
01 Jan 05	$7.9 \pm 1.4$	$8.9 \pm 0.6$	0.87	7.1	4.2
18 Jan 05	$21.5 \pm 2.3$	$28.8 \pm 1.9$	0.94	4.3	4.9

\* SE = standard error.

of total DMS losses in late spring and 53.0% to 88.7% during the summer. DMS photolysis was the main removal process early in November, before the onset of the *P. antarctica* bloom (10 Nov, 73.2%; 14 Nov, 62.8%). Even though Chl *a* was still relatively low ( $1.1 \mu\text{g L}^{-1}$ ) on 18 November, BDMSC dominated over photolysis in the removal of DMS because of the deep ML depth (88 m). Photolysis turnover times for the ML DMS (i.e.,  $1/k_p$ ) ranged from 3.0 d to 81.6 d in the spring and from 5.7 d to 26.7 d in the summer, while BDMSC turnover times for DMS in the ML (i.e.,  $1/k_{bc}$ ) ranged from 4.1 d to 10.5 d and from 1.0 d to 4.0 d in the spring and summer, respectively. The sea-air flux contributed <15% of the total DMS removal on all dates, except for 09 January. Turnover times for ML DMS pools due to sea-air fluxes were generally quite long, ranging from 58 d to 118 d in the spring and from 11 d to 465 d in the summer.

### Discussion

Some of the highest reported seawater DMS concentrations have come from the Ross Sea, with values exceeding  $300 \text{ nmol L}^{-1}$  during the austral spring and summer (DiTullio et al. 2003; Gambaro et al. 2004). However, most of the DMS data from the Antarctic are based on measurements made by sparging unfiltered seawater (DiTullio and Smith 1995; Gambaro et al. 2004; Trevena and Jones 2006), an approach that might overestimate DMS concentrations (see below). DiTullio et al. (2003) recognized the difficulty in measuring DMS in Ross Sea waters dominated by *P. antarctica*, noting that sparging unfiltered samples produced inconsistent results. Wolfe et al. (2000) found that sparging unfiltered samples from the Labrador Sea, where *Phaeocystis pouchetii* was abundant, yielded consistently higher DMS concentrations compared to that obtained by sparging GF/F-filtered samples, suggesting stress-induced production of DMS by plankton during the sparging process. Tests we conducted during the colonial *P. antarctica* bloom in the Ross Sea showed that DMS concentrations in unfiltered seawater were systematically higher than those obtained if the water was filtered through a GF/F filter (Table 1). We also found that GF/F-filtered samples produced higher DMS concentrations than seawater samples that were first screened through a  $20\text{-}\mu\text{m}$  mesh before GF/F filtration ( $20 \mu\text{m} + \text{GF/F}$ ; Table 1) and concentrations obtained using the screening method ( $20 \mu\text{m} + \text{GF/F}$ ) were comparable to results from dialysis samplers (Slide-A-Lyzers; Table 1), which did not require sample filtration. The screening method also compared well with concentrations found using sequential in-line filtration ( $20\text{-}\mu\text{m}$  Nitex mesh followed by a  $3\text{-}\mu\text{m}$  or  $1\text{-}\mu\text{m}$  Nuclepore polycarbonate filter, data not shown) that minimized DMS loss from the sample. Because all samples were handled with procedures that minimized degassing of DMS, differential losses cannot explain the lower DMS concentration in the  $20 \mu\text{m} + \text{GF/F}$  treatment. We conclude, therefore, that DMS concentrations might have been overestimated in some previous studies due to artifacts stemming from the analysis of unfiltered, or inappropriately filtered samples (i.e., direct GF/F filtration) containing *Phaeocystis* sp.

The spring *P. antarctica* bloom in the Ross Sea began in November and was accompanied by substantial increases in surface Chl *a* and DMS concentrations (Fig. 2a,c). DMS

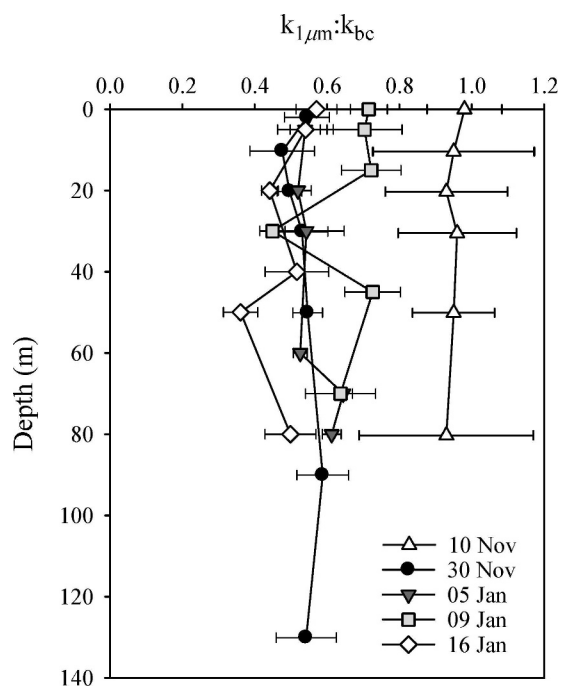


Fig. 7. Vertical profiles of the ratio between  $k_{1\mu\text{m}}$ , the biological DMS consumption rate constant in the fraction  $<1 \mu\text{m}$ , and  $k_{bc}$ , the rate constant in unfiltered water. Horizontal error bars denote the propagated error of the  $k_{1\mu\text{m}} : k_{bc}$ .

concentrations obtained by prefiltering through a 20- $\mu\text{m}$  mesh and then through a GF/F filter (i.e., the method that provided the lowest and the most consistent DMS concentrations) ranged from 0.3  $\text{nmol L}^{-1}$  in early November, before the bloom, to 67.7  $\text{nmol L}^{-1}$  by the end of November. DMS concentrations in summer (3.2–16.8  $\text{nmol L}^{-1}$ ) were well below the springtime peak levels and appeared to decline during the month of January (Fig. 2d). Our finding that surface DMS concentrations in the Ross Sea peaked in the spring is consistent with previous observations of higher DMS concentrations during the exponential growth phase of *Phaeocystis* blooms as compared with the senescence phase (Van Duyl et al. 1998; DiTullio et al. 2003). The maximum DMS concentration reported here was substantially lower than that reported by other studies conducted in this region (DiTullio and Smith 1995; Gambaro et al. 2004), most likely because we minimized artificial release or production of DMS from sensitive plankton. However, interannual variability could also explain the lower concentrations we observed. Nonetheless, DMS concentrations reported in this study are still well above average concentrations reported for most oceanic and coastal areas (Kettle et al. 1999).

BDMSC rates, which are the product of  $k_{bc}$  and the DMS concentration, increased significantly as the spring bloom developed, rising from 0.02  $\text{nmol L}^{-1} \text{d}^{-1}$  on 09 November to 8.8  $\text{nmol L}^{-1} \text{d}^{-1}$  on 28 November. BDMSC rates remained high in the summer ranging from 2.6  $\text{nmol L}^{-1} \text{d}^{-1}$  to 7.3  $\text{nmol L}^{-1} \text{d}^{-1}$ , despite lower DMS concentrations during that time (Fig. 2). Relatively few estimates of BDMSC rates have been made in *Phaeocystis* sp.-dominated waters. In the North Sea, Simó et al. (2000) reported a consumption rate of 122  $\text{nmol L}^{-1} \text{d}^{-1}$  at a DMS concentration of 65  $\text{nmol L}^{-1}$ . This DMS concentration is comparable to values we obtained in late November in the Ross Sea, yet the BDMSC rate obtained in the North Sea was more than an order of magnitude higher than those reported in our study. This disparity may be due to differences in seawater temperature between the Ross Sea ( $-1.8$ – $0.3^\circ\text{C}$ ) and the North Sea ( $14^\circ\text{C}$ ) at the time these studies were carried out, or to methodological differences (see below). DiTullio et al. (2003) reported very high BDMSC rates in the Ross Sea (43–324  $\text{nmol L}^{-1} \text{d}^{-1}$ ) during a *Phaeocystis* bloom, but some of these values came from samples with much higher DMS concentrations (up to 232  $\text{nmol L}^{-1}$ ) than reported here. Both Simó et al. (2000) and DiTullio et al. (2003) used chloroform to determine BDMSC rates, a method that has been shown to overestimate this process (Wolfe and Kiene 1993a; Simó et al. 2000). In addition, DiTullio et al. (2003) sparged unfiltered seawater for DMS analysis. It is, therefore, possible that BDMSC rates were overestimated in the DiTullio et al. and Simó et al. studies because of artifacts associated with the chloroform method or DMS sampling and analysis (Table 1).

The low temperatures characteristic of polar seas have been proposed to be partially responsible for DMS accumulation by limiting BDMSC (Wolfe et al. 1999). During our study, BDMSC rates increased up to 8.8  $\text{nmol L}^{-1} \text{d}^{-1}$  during the spring when surface water temperature

was uniformly low ( $<0.3^\circ\text{C}$ ), and overall there was no relationship between BDMSC rates and temperature. This suggests that temperature per se did not limit or control BDMSC rates. In fact, our BDMSC rates are near the upper end of the BDMSC rates obtained with the  $^{35}\text{S}$ -DMS technique in warmer waters (Table 3). For example, Vila-Costa et al. (2008) reported BDMSC rates ranging from 0.1  $\text{nmol L}^{-1} \text{d}^{-1}$  to 7.7  $\text{nmol L}^{-1} \text{d}^{-1}$  during an annual study conducted in the Mediterranean Sea. On the other hand,  $k_{bc}$  values for BDMSC in the Ross Sea were lower in the spring (0.05–0.21  $\text{d}^{-1}$ ) when water temperatures were  $-1.8$ – $0.3^\circ\text{C}$ , compared to the summer (0.22–0.98  $\text{d}^{-1}$ ) when water temperatures were  $1$ – $1.7^\circ\text{C}$ ; therefore, we cannot rule out a temperature effect on this aspect of DMS turnover.

Results from our BDMSC kinetic experiments showed that  $K_s$  values were lower than the in situ DMS concentrations in the spring but higher than DMS concentrations in the summer. Moreover, in situ BDMSC rates were 70–72% of  $V_m$  in the spring but only 15–47% of  $V_m$  in the summer. In addition, the lowest value of  $V_m$  for BDMSC was found in the spring, when the DMS concentration was relatively high (22.9  $\text{nmol L}^{-1}$ ) and the turnover time due to BDMSC was long (8.2 d). These results suggest that BDMSC was closer to saturation in the spring than in the summer, possibly due to a slow response of the DMS consumers to the rapid increases in DMS concentrations during the spring. This interpretation is consistent with the low turnover rate constants for BDMSC observed during the time of rapid DMS increase, a phenomenon observed previously during bloom development (Zubkov et al. 2004). The range of kinetic parameters for BDMSC we obtained ( $V_m = 7.9$ – $21.5 \text{ nmol L}^{-1} \text{d}^{-1}$ ,  $K_s = 4.0$ – $28.8 \text{ nmol L}^{-1}$ ) is comparable to ranges observed in the Labrador Sea ( $V_m = 9.4$ – $16.1 \text{ nmol L}^{-1} \text{d}^{-1}$ ,  $K_s = 11.2$ – $25.3 \text{ nmol L}^{-1}$ ; Wolfe et al. 1999) and in a temperate coastal system ( $V_m = 0.8$ – $40.6 \text{ nmol L}^{-1} \text{d}^{-1}$ ,  $K_s = 3.9$ – $20.8 \text{ nmol L}^{-1}$ ; Wolfe and Kiene 1993b).

The ML is the most relevant depth horizon regarding DMS cycling because production and loss processes within this layer control the surface DMS concentration and hence its flux to the atmosphere. In our study, BDMSC was the main removal mechanism for ML DMS during the spring and summer, except for two dates in the early spring (10 Nov and 14 Nov) when overall DMS losses were low (Fig. 8). On those early spring dates, optically clear waters allowed deep ultraviolet (UV) light incursion (Kieber et al. 2009) and photolysis was the dominant sink for DMS. Toole et al. (2004) also reported photolysis to be the main removal pathway for DMS in early November in the Southern Ocean north of our study area. Once the Ross Sea bloom started to develop (and DMS concentrations increased), BDMSC was the main removal mechanism for DMS in spite of the relatively long turnover times attributed to BDMSC during November (4.1–10.5 d). Depending on meteorological forcing factors, the sea–air flux can also be responsible for significant DMS loss from surface waters (Simó and Pedrós-Alió 1999). In our study, however, the sea–air flux was only a minor contributor to DMS loss from the ML even on days when winds averaged

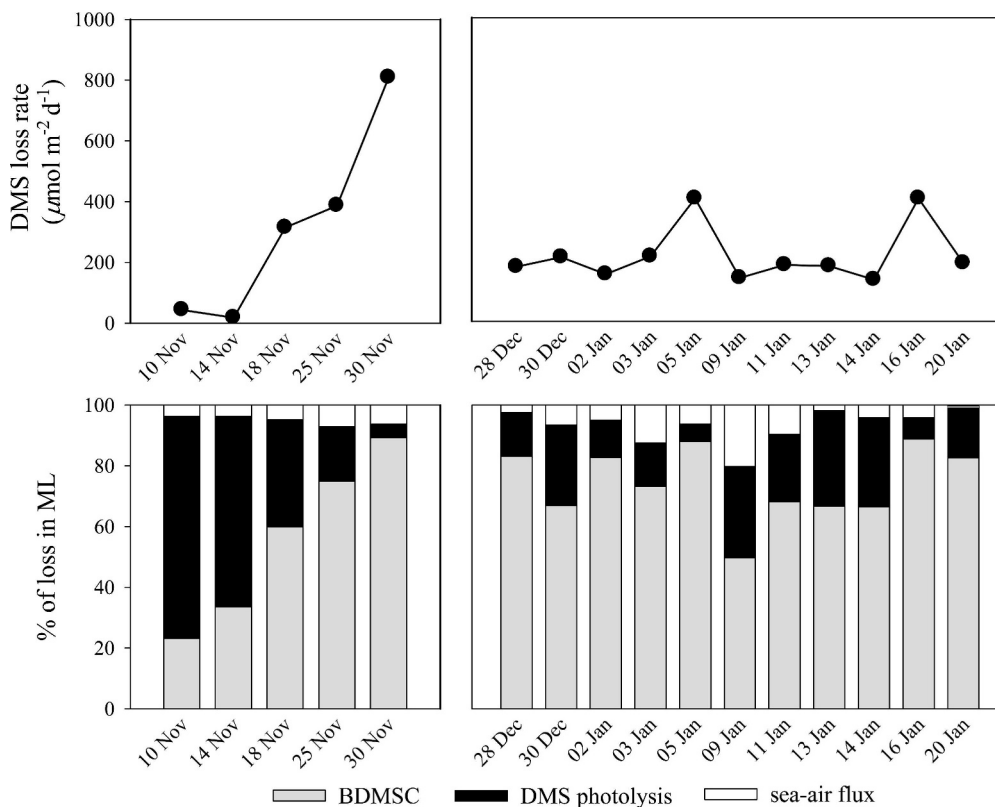


Fig. 8. Upper panels: Time series of the total mixed-layer-integrated DMS loss rates in the Ross Sea, Antarctica. Lower panels: Percent contribution of biological DMS consumption (BDMSC), DMS photolysis, and sea-air flux to total DMS loss rates integrated over the mixed layer for different sampling dates.

$>8 \text{ m s}^{-1}$  (data not shown). During the spring, the relatively slow rates of the three main removal processes are a crucial feature in this system which, when combined with rapid DMS production (DiTullio et al. 2003), sets the stage for high DMS concentrations in the ML. During the summer, rapid turnover of DMS due to BDMSC (turnover times of 1.0–4.0 d) and a shift in the phytoplankton community from *P. antarctica* to low-DMSP-producing diatoms (DiTullio et al. 2003) resulted in lower concentrations than observed in the late spring. Short turnover times

for DMS due to BDMSC have been reported for a variety of locations at different latitudes, such as the North Sea, the Mediterranean, and the Sargasso Sea (Table 3), and taken together with our results from the Ross Sea, this suggests that rapid DMS consumption is a common feature nearly everywhere in the ocean, even in the polar seas.

Several authors have reported a negative effect of UV radiation on BDMSC (Slezak et al. 2001; Toole et al. 2006; Kieber et al. 2007). During our cruises to the Ross Sea, the sun was above the horizon at all times, but light levels were

Table 3. Comparison of mixed-layer biological DMS consumption (BDMSC) rates from different studies that used the  $^{35}\text{S}$ -DMS tracer technique. Also shown is the turnover time of the DMS pool in the ML due to biological consumption ( $\tau_{\text{DMS-Bio}}$ ). The turnover time is the inverse of the BDMSC rate constant ( $k_{\text{bc}}$ ).

Location	Season	DMS (nmol L <sup>-1</sup> )	BDMSC rate (nmol L <sup>-1</sup> d <sup>-1</sup> )	$\tau_{\text{DMS-Bio}}$ (d)	Chl <i>a</i> ( $\mu\text{g L}^{-1}$ )	Study
North Sea	spring summer	4.1±2.2	3.9±1.1	1.0	No data	Zubkov et al. 2002
Northern Ross Sea	spring	0.23–1.5	0.09–0.2	4.9–12	No data	Toole et al. 2004
Dauphin Island, Alabama	spring	1.0	0.8	1.4	4.3	Zubkov et al. 2004
Western Atlantic	spring	0.6–6.4	0.14–1.3	0.9–3.2	0.1–1.1	Toole et al. 2006
Southern Ocean	spring	0.6–27	<0.5–7.5	1–11	No data	Kiene et al. 2007
Sargasso Sea	summer	<3.0	0.2–0.4	7.7–13.6	0.03–0.04	Bailey et al. 2008
Northwest Mediterranean	annual study	0.5–8	0.1–7.7	0.7–>10	0.4–~2.7	Vila-Costa et al. 2008
Ross Sea Polynya	spring	0.3–67.7	0.02–8.8	4.7–18.7	0.1–6.8	this study
	summer	3.2–16.8	2.6–7.3	1.0–4.6	1.8–5.7	this study

relatively low from 19:00 h to 06:00 h. Most of our depth profiles were collected in the morning and we did not find clear evidence of UV inhibition in near-surface samples within the mixed layer. The fairly homogenous in situ BDMSC rate constants found within the ML may have been the product of homogenization due to vertical mixing during the low-light hours prior to sampling, in situ recovery of the microbial community during the hours with low light levels, or recovery during the 4–8-h dark incubations with  $^{35}\text{S}$ -DMS. Although no patterns were observed within the ML, we did observe that BDMSC rate constants were consistently lower in the ML than below it during the summer (Fig. 4). Toole et al. (2006) also observed this pattern at different stations in the western Atlantic Ocean, and attributed it to an inhibitory effect of UV radiation on BDMSC in the surface layer, although they also recognized that other factors (e.g., different community composition in the two layers) could account for this difference. Further research will be needed to firmly establish whether UV or other factors are responsible for the pattern of BDMSC rate constants that are observed with depth in the Ross Sea.

Detailed size-fractionation studies showed that BDMSC was mostly carried out in the size fraction  $<1\ \mu\text{m}$  (i.e., free-living bacteria, 36–73%; Fig. 7) and  $>8\ \mu\text{m}$  (32–37%), except very early in the season before the development of the bloom, when free-living bacteria ( $<1\ \mu\text{m}$ ) were responsible for 95% of the consumption. The contribution of free-living bacteria to BDMSC in the Ross Sea is somewhat greater than what was found in the Sargasso Sea, where, following the same analytical procedures as in this study, free-living bacteria ( $<1\ \mu\text{m}$ ) were responsible for a low percentage (18–34%) of the BDMSC carried out in unfiltered water (D. A. del Valle unpubl.). BDMSC associated with the particulate fractions ( $>8\ \mu\text{m}$ ) could have been carried out by particle-associated bacteria, but it is also possible that phytoplankton were responsible for a fraction of the consumption in the nonfiltered samples. Phytoplankton species such as *Emiliania huxleyi* strain CCMP 373 and *Alexandrium tamarese* strain CCMP 1771 have been shown to consume nanomolar levels of DMS in cultures (Wolfe et al. 2002). However, there are no reports of consumption of DMS by phytoplankton in a natural system. The fact that increases in surface Chl *a* had no effect on surface BDMSC rate constants during the spring (Fig. 2), and the lack of correlation between these two variables during both the spring and summer, argues against a significant role of phytoplankton in consuming DMS in this system. Several studies have assumed that free-living bacteria are mainly responsible for DMS consumption in seawater. Based on this assumption, they used filtered seawater to capture the bacterial community carrying out BDMSC (Scarratt et al. 2000; Slezak et al. 2001; Vila-Costa et al. 2006). Because our results indicate that free-living bacteria contribute only a portion of the total BDMSC activity, and because free-living and attached bacteria can have marked taxonomical and physiological differences (Iriberry et al. 1990; Delong et al. 1993), caution should be applied when deriving conclusions about DMS

consumption if just the free-living bacterial fraction is sampled.

This work represents the first detailed study of the seasonal variation of BDMSC and its role as a removal mechanism for DMS in the Antarctic. BDMSC was the dominant loss process for DMS in the surface mixed layer of the Ross Sea, even during the spring bloom when DMS concentrations increased substantially and when BDMSC rates were close to substrate saturation. Using improved methodology for the quantification of DMS in *Phaeocystis*-dominated waters, we found that peak DMS concentrations in the Ross Sea were 5–7-fold lower than reported previously. Nonetheless, Ross Sea DMS concentrations in the early bloom were very high (up to  $67.7\ \text{nmol L}^{-1}$ ) relative to the world-wide ocean average of  $5.5\ \text{nmol L}^{-1}$  (median =  $2.2\ \text{nmol L}^{-1}$ ; Kettle et al. 1999). Relatively slow biological turnover of DMS contributed to the build up of DMS concentrations during late November. During the summer, DMS concentrations were much lower ( $3.2$ – $16.8\ \text{nmol L}^{-1}$ ), but still relatively high compared to other areas of the ocean. Fast biological turnover of DMS in the summer was a major factor preventing even higher DMS concentrations at that time.

#### Acknowledgments

Funding was provided by grants from the National Science Foundation (OPP-0230497 to R. P. Kiene and OPP-0230499 to D. J. Kieber). D. A. del Valle was partially supported by a student fellowship from the University of South Alabama. We appreciate the help provided by Brian Jones, Doris Slezak, Laura Linn, Hyakubun Harada, and Alison Rellinger in collection of ancillary data. Thanks also to the captain and crew of the RVIB *N.B. Palmer*, to the support staff of Raytheon Polar Services, and to Wade Jeffrey, the Chief Scientist on the November 2005 cruise. Finally, we thank two anonymous reviewers for helpful comments and suggestions.

#### References

- ARRIGO, K. R., A. M. WEISS, AND W. O. SMITH. 1998. Physical forcing of phytoplankton dynamics in the southwestern Ross Sea. *J. Geophys. Res.* **103**: 1007–1021.
- BAILEY, K. E., AND OTHERS. 2008. Estimation of dimethylsulfide production in Sargasso Sea Eddies. *Deep-Sea Res. Part II* **55**: 1491–1504.
- BATES, T. S., AND OTHERS. 1994. The cycling of sulfur in surface sea water of the Northeast Pacific. *J. Geophys. Res.* **99**: 7835–7843.
- CHARLSON, R. J., J. E. LOVELOCK, M. O. ANDREAE, AND S. G. WARREN. 1987. Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate. *Nature* **326**: 655–661.
- DELONG, E., D. FRANKS, AND A. ALLDREDGE. 1993. Phylogenetic diversity of aggregate-attached vs. free-living marine bacterial assemblages. *Limnol. Oceanogr.* **38**: 924–934.
- DEL VALLE, D. A., D. J. KIEBER, AND R. P. KIENE. 2007. Depth-dependent fate of biologically-consumed dimethylsulfide in the Sargasso Sea. *Mar. Chem.* **103**: 197–208.
- DI TULLIO, G. R., D. R. JONES, AND M. E. GEESEY. 2003. Dimethylsulfide dynamics in the Ross Sea during austral summer, p. 279–294. In G. R. DiTullio and R. G. Dunbar [eds.], *Biogeochemistry of the Ross Sea*. Antarctic research series. American Geophysical Union.

- , AND W. O. SMITH. 1995. Relationship between dimethylsulfide and phytoplankton pigment concentrations in the Ross Sea, Antarctica. *Deep-Sea Res. Part I* **42**: 873–892.
- GABRIC, A. J., P. A. MATRAI, AND M. VERNET. 1999. Modelling the production and cycling of dimethylsulphide during the vernal bloom in the Barents Sea. *Tellus* **51B**: 919–937.
- GAMBARO, A., AND OTHERS. 2004. Temporal evolution of DMS and DMSP in Antarctic coastal sea water. *Int. J. Environ. Anal. Chem.* **84**: 401–412.
- IRIBERRI, J., M. UNANUE, B. AYO, I. BARCINA, AND L. EGEA. 1990. Bacterial production and growth rate estimation from [3H] thymidine incorporation for attached and free-living bacteria in aquatic systems. *Appl. Environ. Microbiol.* **56**: 483–487.
- KETTLE, A. J., AND M. O. ANDREAE. 2000. Flux of dimethylsulfide from the oceans: A comparison of updated data sets and flux models. *J. Geophys. Res.* **105**: 26793–26808.
- , AND OTHERS. 1999. A global database of sea surface dimethylsulfide (DMS) measurements and a procedure to predict sea surface DMS as a function of latitude, longitude, and month. *Glob. Biogeochem. Cycles* **13**: 399–444.
- KIEBER, D. J., D. A. TOOLE, J. J. JANKOWSKI, R. P. KIENE, G. R. WESTBY, D. A. DEL VALLE, AND D. SLEZAK. 2007. Chemical “light meters” for photochemical and photobiological studies. *Aquat. Sci.* **69**: 360–376.
- , AND R. P. KIENE. 2009. Chromophoric organic matter cycling during a Ross Sea *Phaeocystis antarctica* bloom, p. 319–334. *In* I. Krupnik, M. A. Lang and S. E. Miller [eds.], *Smithsonian at the Poles: Contributions to International Polar Year Science*. Smithsonian Institution Scholarly Press.
- KIENE, R. P., AND T. S. BATES. 1990. Biological removal of dimethyl sulphide from seawater. *Nature* **345**: 702–705.
- , AND OTHERS. 2007. Distribution and cycling of dimethylsulfide, dimethylsulfoniopropionate, and dimethylsulfoxide during spring and early summer in the Southern Ocean south of New Zealand. *Aquat. Sci.* **69**: 305–319.
- , AND L. J. LINN. 2000. Distribution and turnover of dissolved DMSP and its relationship with bacterial production in the Gulf of Mexico. *Limnol. Oceanogr.* **45**: 849–861.
- , AND S. K. SERVICE. 1991. Decomposition of dissolved DMSP and DMS in estuarine waters: Dependence on temperature and substrate concentration. *Mar. Ecol. Prog. Ser.* **76**: 1–11.
- , AND D. SLEZAK. 2006. Low dissolved DMSP concentrations in seawater revealed by small volume gravity filtration and dialysis sampling. *Limnol. Oceanogr. Methods* **4**: 80–95.
- LISS, P. S., G. MALIN, S. TURNER, AND P. HOLLIGAN. 1994. Dimethyl sulphide and *Phaeocystis*: A review. *J. Mar. Syst.* **5**: 41–53.
- NIGHTINGALE, P. D., G. MALIN, C. S. LAW, A. J. WATSON, P. S. LISS, AND M. I. LIDDICOAT. 2000. In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers. *Glob. Biogeochem. Cycles* **14**: 373–387.
- ROLL, H. 1965. *Physics of the marine atmosphere*. Academic Press.
- SCARRATT, M. G., AND OTHERS. 2000. Production and consumption of dimethylsulfide (DMS) in North Atlantic waters. *Mar. Ecol. Prog. Ser.* **204**: 13–26.
- SIMÓ, R. 2001. Production of atmospheric sulfur by oceanic plankton: Biogeochemical, ecological and evolutionary links. *Trends Ecol. Evol.* **16**: 287–294.
- . 2004. From cells to globe; approaching the dynamics of DMS(P) in the ocean at multiple scales. *Can. J. Fish. Aquat. Sci.* **61**: 673–684.
- , AND C. PEDRÓS-ALIÓ. 1999. Short-term variability in the open ocean cycle of dimethylsulfide. *Glob. Biogeochem. Cycles* **13**: 1173–1181.
- , G. MALIN, AND J. O. GRIMALT. 2000. Biological turnover of DMS, DMSP and DMSO in contrasting open-sea waters. *Mar. Ecol. Prog. Ser.* **203**: 1–11.
- SLEZAK, D., A. BRUGGER, AND G. J. HERNDL. 2001. Impact of solar radiation on the biological removal of dimethylsulfoniopropionate and dimethylsulfide in marine surface waters. *Aquat. Microb. Ecol.* **25**: 87–97.
- SMITH, D. C., AND F. AZAM. 1992. A simple, economical method for measuring bacterial protein synthesis rates in sea water using <sup>3</sup>H-Leucine. *Mar. Microb. Food Webs* **6**: 107–114.
- STEFELS, J., AND W. H. M. VAN BOEKEL. 1993. Production of DMS from dissolved DMSP in axenic cultures of the marine phytoplankton species *Phaeocystis* sp. *Mar. Ecol. Prog. Ser.* **97**: 11–18.
- STEINKE, M., C. DANIEL, AND G. O. KIRST. 1996. DMSP lyase in marine micro- and macroalgae: Intraspecific differences in cleavage activity, p. 317–324. *In* R. P. Kiene, P. T. Visscher, M. D. Keller and G. O. Kirst [eds.], *Biological and environmental chemistry of DMSP and related sulfonium compounds*. Plenum.
- STRICKLAND, J. D. H., AND T. R. PARSONS. 1972. *A practical handbook of seawater analysis*. Bull. Fish. Res. Bd. Canada.
- TOOLE, D. A., D. J. KIEBER, R. P. KIENE, D. A. SIEGEL, AND N. B. NELSON. 2003. Photolysis and the dimethylsulfide (DMS) summer paradox in the Sargasso Sea. *Limnol. Oceanogr.* **48**: 1088–1100.
- , ———, E. M. WHITE, J. BISGROVE, D. A. DEL VALLE, AND D. SLEZAK. 2004. High dimethylsulfide photolysis rates in nitrate-rich Antarctic waters. *Geophys. Res. Lett.* **31**: L11307, doi:10.1029/2004GL019863.
- , D. SLEZAK, R. P. KIENE, D. J. KIEBER, AND D. A. SIEGEL. 2006. Effects of solar radiation on dimethylsulfide cycling in the western Atlantic Ocean. *Deep-Sea Res. Part I* **53**: 136–153.
- TREVENA, A. J., AND G. B. JONES. 2006. Dimethylsulphide and dimethylsulfoniopropionate in Antarctic sea ice and their release during sea ice melting. *Mar. Chem.* **98**: 210–222.
- VAN DUYL, F. C., W. W. C. GIESKES, A. J. KOP, AND W. E. LEWIS. 1998. Biological control of short-term variations in the concentration of DMSP and DMS during a *Phaeocystis* spring bloom. *J. Sea Res.* **40**: 3–4.
- VILA-COSTA, M., D. A. DEL VALLE, J. M. GONZÁLEZ, D. SLEZAK, R. P. KIENE, O. SÁNCHEZ, AND R. SIMÓ. 2006. Phylogenetic identification and metabolism of marine dimethylsulfide-consuming bacteria. *Environ. Microbiol.* **8**: 2189–2200.
- , R. P. KIENE, AND R. SIMÓ. 2008. Seasonal variability of the dynamics of dimethylated sulfur compounds in a coastal northwest Mediterranean site. *Limnol. Oceanogr.* **53**: 198–211.
- WOLFE, G. V., AND R. P. KIENE. 1993a. Radioisotope and chemical inhibitor measurements of dimethyl sulfide consumption rates and kinetics in estuarine waters. *Mar. Ecol. Prog. Ser.* **99**: 261–269.
- , AND ———. 1993b. Effects of methylated, organic, and inorganic substrates on microbial consumption of dimethyl sulfide in estuarine waters. *Appl. Environ. Microbiol.* **59**: 2723–2726.
- , M. LEVASSEUR, G. CANTIN, AND S. MICHAUD. 1999. Microbial consumption and production of dimethyl sulfide (DMS) in the Labrador Sea. *Aquat. Microb. Ecol.* **18**: 197–205.

- , ———, ———, AND ———. 2000. DMSP and DMS dynamics and microzooplankton grazing in the Labrador Sea: Application of the dilution technique. *Deep-Sea Res. Part I* **47**: 2243–2264.
- , S. L. STROM, T. R. HOLMES, AND M. B. OLSON. 2002. Dimethylsulfoniopropionate cleavage by marine phytoplankton in response to mechanical, chemical, or dark stress. *J. Phycol.* **38**: 948–960.
- ZUBKOV, M. V., B. M. FUCHS, S. D. ARCHER, R. P. KIENE, R. AMANN, AND P. H. BURKILL. 2002. Rapid turnover of dissolved DMS and DMSP by defined bacterioplankton communities in the stratified euphotic zone of the North Sea. *Deep-Sea Res. II* **49**: 3017–3038.
- , L. J. LINN, R. AMANN, AND R. P. KIENE. 2004. Temporal patterns of biological dimethylsulfide (DMS) consumption during laboratory-induced phytoplankton bloom cycles. *Mar. Ecol. Prog. Ser.* **271**: 77–86.

*Associate editor: Mikhail V. Zubkov*

*Received: 25 March 2008*  
*Accepted: 29 September 2008*  
*Amended: 11 December 2008*