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Dimethylsulphide and dimethylsulphoniopropionate in Antarctic sea ice and their release during sea ice melting

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Abstract

This study presents concentrations of dimethylsulphide (DMS) and its precursor compound dimethylsulphoniopropionate (DMSP) in a variety of sea ice and seawater habitats in the Antarctic Sea Ice Zone (ASIZ) during spring and summer. Sixty-two sea ice cores of pack and fast ice were collected from twenty-seven sites across an area of the eastern ASIZ (64°E to 110°E; and the Antarctic coastline north to 62°S). Concentrations of DMS in 81 sections of sea ice ranged from <0.3 to 75 nM, with an average of 12 nM. DMSP in 60 whole sea ice cores ranged from 25 to 796 nM and showed a negative relationship with ice thickness ($y = 125 x^{-0.8}$). Extremely high DMSP concentrations were found in 2 cores of rafted sea ice (2910 and 1110 nM). The relationship of DMSP with ice thickness (excluding rafted ice) suggests that the release of large amounts of DMSP during sea ice melting may occur in discrete areas defined by ice thickness distribution, and may produce 'hot spots' of elevated seawater DMS concentration of the order of 100 nM. During early summer across a 500 km transect through melting pack ice, elevated DMS concentrations (range 21–37 nM, mean 31 nM, $n = 15$) were found in surface seawater. This band of elevated DMS concentration appeared to have been associated with the release of sea ice DMS and DMSP rather than in situ production by an ice edge algal bloom, as chlorophyll a concentrations were relatively low (0.09–0.42 µg l^{-1}). During fast ice melting in the area of Davis station, Prydz Bay, sea ice DMSP was released mostly as extracellular DMSP, since intracellular DMSP was negligible in both hyposaline brine (5 ppt) and in a melt water lens (4–5 ppt), while extracellular DMSP concentrations were as high as 149 and 54 nM, respectively in these habitats. DMS in a melt water lens was relatively high at 11 nM. During the ice-free summer in the coastal Davis area, DMS concentrations in surface seawater were highest immediately following breakout of the fast ice cover in late December (range 5–14 nM), and then remained at relatively low concentrations through to late February (<0.3–6 nM). These measurements support the view that the melting of Antarctic sea ice produces elevated seawater DMS due to release of sea ice DMS and DMSP.

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1. Introduction

Dimethylsulphide (DMS) is the major volatile sulphur compound in the oceans and is climatically important since it affects the radiative properties of clouds

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through its atmospheric oxidation products. Its biochemical precursor is dimethylsulphoniopropionate (DMSP), which is ubiquitous in the oceans where it is produced by several classes of phytoplankton (see Malin et al., 1994). DMS production from DMSP occurs predominantly via enzymatic cleavage in surface waters (e.g., Malin and Kirst, 1997; Stefels, 2000). Production and accumulation of DMS is intricately linked with food-web dynamics (e.g., Ledyard and Dacey, 1996; Archer et al., 2002). The true function of DMS is uncertain (Stefels, 2000). It may simply be a physiological waste product associated with DMSP (Malin and Kirst, 1997) or a key component in the altruistic behaviour of marine algal communities that acts, via ocean–atmosphere feedback (see Malin et al., 1994) to maintain the radiative balance of the earth and create conditions optimal for photosynthetic life (Simó, 2001). DMS may also function as an antioxidant, which protects cells during conditions of oxidative stress (i.e., increased UV radiation, CO_2 and/or Fe limitation; Sunda et al., 2002).

The function of DMSP in algal cells is reported to include a compatible solute, which contributes to protection against high salinity (e.g., Dickson and Kirst, 1986) and freezing (Karsten et al., 1996), a multifunctional defence precursor for the production of acrylic acid (produced by DMSP cleavage) (Wolfe et al., 1997), a regulatory coupling mechanism between assimilatory sulphate and nitrate reduction (Stefels, 2000), and as an antioxidant (Sunda et al., 2002).

The relative ratios of intracellular DMSP (DMSPp), extracellular DMSP (DMSPd) and dissolved DMS in surface waters are influenced by the life stages of an algal community and the composition of the microbial food web. DMSPp generally dominates during exponential and stationary growth phases while DMSPd and DMS concentrations typically increase during senescence, increased grazing pressure (e.g., Wolfe et al., 1997; Archer et al., 2002), bacterial activity (Visscher et al., 1992; Ledyard and Dacey, 1996), and the presence of viruses (Malin et al., 1994). The release of DMSPd by healthy algal cells may occur in response to decreasing salinity (Stefels and Dijkhuizen, 1996). DMS production occurs via enzymatic cleavage of DMSP by either algal or bacterial DMSP-lyase enzymes (Visscher et al., 1992; Stefels and Dijkhuizen, 1996). Bacterial activity accounts for the majority of DMSPd and DMS turnover, with consumption being the major process (Visscher et al., 1992; Archer et al., 2002). DMS production is generally a small component of DMSP turnover (<20%, e.g., Ledyard and Dacey, 1996; Kiene and

Linn, 2000; Archer et al., 2002), though the yield of DMS may vary seasonally (Ledyard and Dacey, 1996; Archer et al., 2002) or with mixed layer depth (Simó and Pedrós-Alió, 1999).

Antarctic sea ice contains very large but variable concentrations of DMSP (Kirst et al., 1991; Turner et al., 1995; Curran et al., 1998; DiTullio et al., 1998; Trevena et al., 2000, 2003; Gambaro et al., 2004). Concentrations from across seven sea ice studies, summarised by Trevena et al. (2003), ranged from less than 5 to around 1660 nM, with averages for each study of the order of 100 to 300 nM. The large variability in sea ice DMSP has been attributed mostly to the patchy distribution of ice algal biomass and its variable taxonomic composition (Kirst et al., 1991; Turner et al., 1995; Curran et al., 1998; DiTullio et al., 1998; Trevena et al., 2000, 2003). Considering that the development of sea ice algal assemblages is intrinsically linked with ice growth and history (Ackley and Sullivan, 1994), it is plausible that DMSP concentrations thus may vary characteristically between sea ice of different thicknesses (see Trevena et al., 2000, 2003). It is thought the release of sea ice DMSP during annual ice melting is, in part, responsible for elevated concentrations of DMSP and DMS in seawater (Fogelqvist, 1991; Kirst et al., 1991; Curran et al., 1998; DiTullio et al., 1998; Curran and Jones, 2000). Kirst et al. (1991) suggested that the release of large amounts of DMSP during Antarctic sea ice melting could produce high concentrations of seawater DMS with the potential to effect local climate. In Arctic sea ice, Levasseur et al. (1994) reported extremely high DMSP (up to 90 μM) and suggested its release following ice melting could produce a one day pulse of DMS flux ten times higher than the average summer flux. However, we have little knowledge of the release and transformation processes affecting the fate of sea ice DMS and DMSP during sea ice melting (Levasseur et al., 1994; Trevena et al., 2003).

In this study we report the first DMS concentrations in Antarctic sea ice and relate these to concentrations of total DMSP (DMSPt = dissolved DMSP + particulate DMSP) and chlorophyll a (Chl a). We make a preliminary characterisation of sea ice DMSP concentration as a function of ice thickness and report DMSP and DMS concentrations during sea ice melting from different pack and fast ice habitats along with seawater concentrations at a coastal site during the ice-free summer. We investigate the dynamics of DMSP and DMS in sea ice and surface seawater during sea ice

Table 1
Sea ice core sample site number and name replicate cores collected and ice thickness range

Site number	Replicate cores	Ice thickness (m)
1	1	2.4
2	3	0.3–0.6
3	2	1.4–1.9
4	2	0.5–0.6
5	2	0.4
6	3	0.6
7	2	0.9–1.0
8	2	0.7
9	3	1.0–1.2
10	3	0.6–0.7
11	2	0.5
12	3	0.2–0.3
13	4	0.3–1.8
14	3	1.4–2.2
15	2	1.7–1.8
16	2	1.7–1.8
17	2	1.5–1.7
18	3	1.0
19	3	0.8–1.0
20	3	0.9
21	2	1.6–1.7
22	1	1.9
23	1	1.5
24	1	1.7
25	1	0.8
26	3	0.8–0.9
27	3	1.5–1.6

Site numbers refer to locations shown in Fig. 1.

melting and summarise and discuss reported concentrations in Antarctic waters.

2. Methods

2.1. Study sites and sampling

Sixty two sea ice cores were collected from twenty seven sites across an area of the eastern ASIZ extending between 64°E and 110°E, and the Antarctic coastline north to 62°S (Table 1, Fig. 1). Sea ice cores were collected during late October 1997 and mid November 1998 using either a 12 or 7.5 cm diameter SIPRE corer. Cores were wrapped in black polythene plastic and stored horizontally at −20 °C until processing (within 2 weeks). Replicate cores collected within a site were within an area of approximately 2 m². In the fast ice area around Davis station, and Prydz Bay, during the period of ice melting in late November through December 2000, sea ice brine, under-ice seawater, surface melt-pool water and tide crack seawater were collected. Brine was allowed to drain into 0.5 m drill holes for 15 min and then collected directly into plastic bottles with no headspace. Under-ice seawater was collected through a core hole using a submersible pump into a 25 l plastic container, which was then sub-sampled in the laboratory. Water from surface melt-pools and tide cracks were collected directly into 1 l glass bottles with no headspace. During 2 days in mid-December 1998, surface seawater was collected from a north–south transect (62–66°S) at approximately 75°E (V498 transect; Fig. 1) through the melting pack ice edge using a stainless steel bucket cast from the lower deck of *RV Aurora Australis*. In the Davis area during late December 2000 through February 2001, surface seawater was collected using either a stainless steel bucket cast from the shore or by submerging plastic 1 l bottles from an inflatable rubber boat. Seawater collected by bucket was gently transferred into 1 l bottles, leaving no headspace. All bottled samples were returned to the laboratory within 1 h for processing. Replicate samples from a site were obtained with separate casts.

2.2. Sample processing

Sea ice cores were cut into 0.1 m depth sections and then approximately 1/8 vertical portions with a stainless steel hand saw. For DMSPt preservation, portions were thawed at pH 1, by the addition of 2 ml 1 : 5 v/v
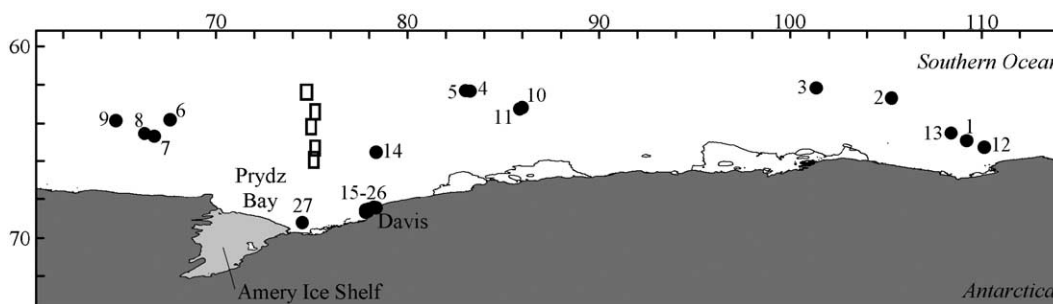

Fig. 1. Sample site locations for sea ice cores (filled circles), and surface seawater collected during V498 transect (open squares) in eastern Antarctica. [For each sea ice site number, Table 1 provides details of the number of replicate cores collected and ice thickness].

Table 2
DMS (P) concentrations (nM) reported in Antarctic surface waters (up to 10 m depth) during October to January

Location	Sampling period	DMSPp	DMSPd	DMS (nM)	Study
Davis area	Dec			54 (48–68)	Deprez et al. (1986)[e]
Davis area	Dec–Jan		(1–100)[c]	(1–290)	Gibson et al. (1990)[e]
Weddell Sea	Dec–Feb			88 (69)[d]	Fogelqvist (1991)
Antarctic Peninsula (coastal)	Nov	2 (0.7–6)[b1]		2 (0.4–9)[b1]	DiTullio and Smith (1993)
Antarctic Peninsula	Dec	(<1–75)		(0.4–250)	Kirst et al. (1993)
Davis area	Nov			2 (1)	McTaggart and Burton (1992)[e]
	Dec		95 (72)	28 (24)	
	Jan		214 (69)	91 (30)	
Bellingshausen Sea	Oct–Nov			55 (23–150)	Crocker et al. (1995)
Drake Passage and Bellingshausen Sea	Oct–Dec	26 (1–28)	12 (1–28)	2 (0.2–27)	Turner et al. (1995)
Ross Sea	Feb			(<1–ca100)	DiTullio and Smith (1995)
Ross Sea	Dec–Jan			(10–340)	DiTullio (1996)
Southern Ocean					Curran (1997)
44–66°S 61–147°E[a]	Jan–Feb	10 (0.5–89)	7 (0.4–32)		
62–66°S 110–150°E	Jan	12 (<0.4–18)	10 (2–58)	7 (1–22)[b3]	
Ross Sea	Feb	(1–10)		(10–97)	DiTullio and Smith (1997)
Terra Nova Bay	Dec–Jan	(<10–150)[b1,b2,c*]		(<10–480)[b1,b2]	Gambaro et al. (2004)
Sea ice	Nov			12 (nd–75)	This work
V298 site[f]	Nov			16 (8–30)	
V498 transect	Dec			31 (21–37)	
Davis area	Dec–Feb	103 (21–303)	32 (6–103)	3 (0.4–14)	

Average (range or standard deviation).
nd=not detected, <0.3 nM.
a) 25% of data set from waters 44–62°S.
b) Selected data for (1) 0–10 m water depth, (2) under–ice seawater, and (3) latitude and month.
c) Estimated from figure, *DMSPt.
d) 0–50 m water depth.
e) Samples treated with mercuric chloride.
f) Surface seawater collected at 62.82°S, 107.22°E on 10th November 1998.

HCl: filtered seawater (0.7 μm), at ambient room temperature. Seawater and brine samples for DMSP were acidified to pH 1 by the addition of a few drops of HCl (conc. 32%). For DMSPd, the sample was gently filtered through a 0.45 μm Sartorius filter before acidification. Samples were stored for up to 4 months in amber glass vials. DMSPp was calculated as the difference between DMSP and DMSPd concentrations. Storage of samples for DMSP analysis indicated samples could be stored up to one year without loss.

For DMS, selected depth portions were broken into smaller pieces and quickly sealed in a purge chamber to thaw at pH 1 (as for DMSP). Two different purge chambers were used: a silanised glass chamber with a ground glass lid, developed for seawater DMS measurements (Curran et al., 1998); or a Teflon container with a wide mouth screw lid, modified for use as a sea ice purge chamber. Seawater or melt-pool water samples were poured gently into a purge chamber, and acidified to pH 1 with 4 drops of HCl (conc. 32%). The liquid samples (50–80 ml) were purged of DMS using nitrogen gas at a flow of 50–100 ml/min for 20 min. DMS was chemisorbed onto gold sputter coated glass wool in Pyrex glass tubes (known as 'gold tubes'; see also Curran et al., 1998) and stored for up to 4 months. Chl a was collected from a 1/2 vertical portion of ice thawed approximately 1:1 v/v with filtered seawater (0.7 μm). Particulate material was filtered (<0.5 atm.) onto a Whatman GF/F syringe (13 mm diam.) and stored in liquid nitrogen for up to 10 months.

2.3. Analysis

The gas chromatograph/flame photometric detection system used for DMS(P) analysis is described by Trevena et al. (2000). DMSP was analysed as DMS fol-
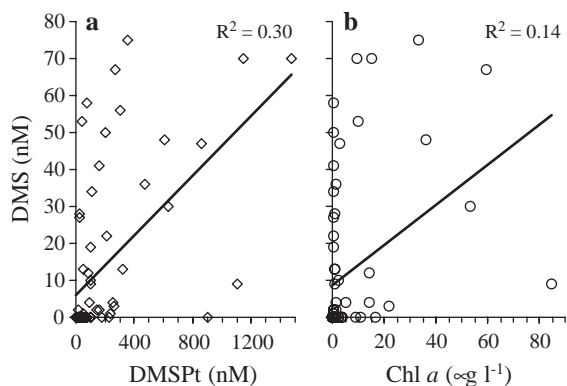
Fig. 2. DMS concentrations in sea ice sections plotted against (a) DMSPt and (b) Chl *a*.

lowing cold alkali cleavage (10 M NaOH) of DMSP. The resultant DMS was purged from the sample aliquot (100–4000 μl) using high purity helium or nitrogen gas (50 ml/min) for 15 min and concentrated by cryogenic trapping (Teflon sample loop in liquid nitrogen, −196 °C). DMS was desorbed from a 'gold tube' at 400 °C (see Curran et al., 1998) and purged and trapped as described above. DMS eluted at around 0.8 and 5.8 min, from a polydimethylsiloxane capillary column (130 °C) or a Poropak Q 80/100 mesh (180 °C) column, respectively. Quantification was achieved from an external calibration equation, obtained using DMSP standard (0.47 ng S/100 μl) injections analysed in an analogous procedure to DMSP. The precision for DMS(P) analysis was ± 10%.

Chl *a* was analysed according to the method of Wright et al. (1996) using the HPLC system described by Trevena et al. (2000). Chl *a* was detected at 665 nm and quantified using an internal standard, *trans*-B-apo-8′-carotenal (Fluka) at 140 ng per sample, and identified by comparison of retention time and spectrum with a "standard mixture" containing Chl *a* (Jeffrey, 1997).

Salinity was measured using a hand held sodium refractometer that had been zeroed using Millipore water.

3. Results

3.1. DMS in sea ice

DMS concentrations in 81 sea ice sections ranged from below detection limit (<0.3 nM) to 75 nM, with an average concentration of 12 nM (Table 2). The distribution of DMS concentrations within the data set was skewed towards low values, a pattern also observed for DMSP concentrations in sea ice sections ($n=658$, data

not shown). Concentrations were below detection limit in more than half the ice sections (57%) and in the range 1–10 nM in 17%. The distribution 'tail' comprised approximately one quarter of the ice sections (26%) with DMS concentrations ranging from 11–75 nM.

A plot of DMS and DMSP concentrations (Fig. 2a) shows the linear relationship between DMS and DMSP was poor ($R^2=0.30$). Most ice sections (71%) with high DMS (>10 nM) had relatively low DMSP concentrations (<400 nM). When DMS was plotted against Chl *a* (Fig. 2b) the correlation was also poor ($R^2=0.14$) due to over half (57%) of the ice sections containing high DMS (>10 nM) and relatively low Chl *a* (<5 μg l^{-1}).

3.2. DMSP and sea ice thickness

Average sea ice DMSP concentrations reported here are for whole cores, obtained from depth profiles with 0.1 m resolution. In sixty of the sea ice cores the DMSP concentration decreased rapidly with increasing ice thickness to around 0.70 m, then continued to decrease more gradually up to 2.4 m (Fig. 3). The best fit to describe the relationship was provided by the exponential equation $y=125 x^{-0.8}$ ($R^2=0.38$). These cores were sorted into five ice thickness categories and the category average DMSP decreased with increasing ice thickness (Table 3). DMSP in young ice was significantly greater (Bonferroni, $P<0.05$) than in medium and thick ice but not thin ice.

For two sea ice cores in the thick ice category, DMSP concentrations were more than five times greater (2910 and 1110 nM) than for the other twenty cores in the same category (25–210 nM). As these two cores constituted outlier points in the data set, they have been excluded from the data in Fig. 3 and Table 3. These two
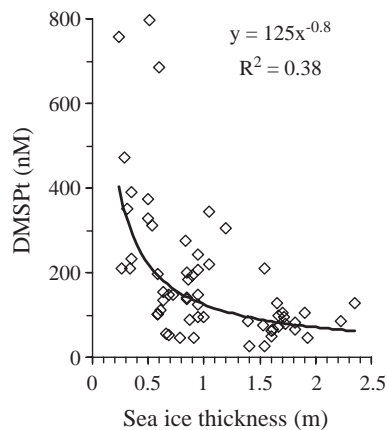

Fig. 3. DMSPt concentrations and ice thickness for 60 sea ice cores of pack and fast ice.

Table 3
Average DMSP concentrations in five ice thickness categories

Category	Ice thickness (m)	No. cores	DMSP (nM)		
			Average	Range	Std dev
Young ice	0.15–0.30	3	480	210–759	275
First stage thin ice[a]	0.30–0.50	4	296	209–389	88
Second stage thin ice[a]	0.50–0.70	14	253	51–796	230
Medium ice	0.70–1.20	19	171	45–343	83
Thick ice	>1.20	20[b]	85	25–210	41

[a] Subgroups of thin first year ice.
[b] Excludes 2 rafted sea ice cores (see text for details).

cores were identified as being rafted sea ice based on deformation of floes in the sampling area and a 'slush ice' cavity within both cores. In addition, the ice thickness of four replicate cores collected at this site varied greatly (site 13; Table 1) and such variability in ice thickness is characteristic of rafted ice floes. The extremely high DMSP in the rafted ice cores was due to very high concentrations found in the interior 'slush ice' layer (1057–13525 nM) and bottom ice (4669–7632 nM) (Fig. 4). Parallel profiles of Chl *a* concentrations, were also very high at these depths (10–50 μg l⁻¹).

3.3. DMS(P) during sea ice melting and summer

The V498 transect through the melting ice edge during mid December (Fig. 5) covered some 500 km during which surface seawater temperatures increased sharply at around 64.5°S (−1.3 to −0.4 °C), coinciding with a decrease in the total ice cover from 60–80% in the colder waters (−1.3 to −1.4 °C) to the south, to less than 30%
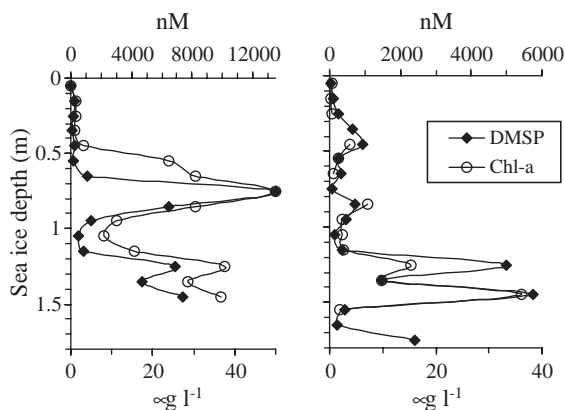
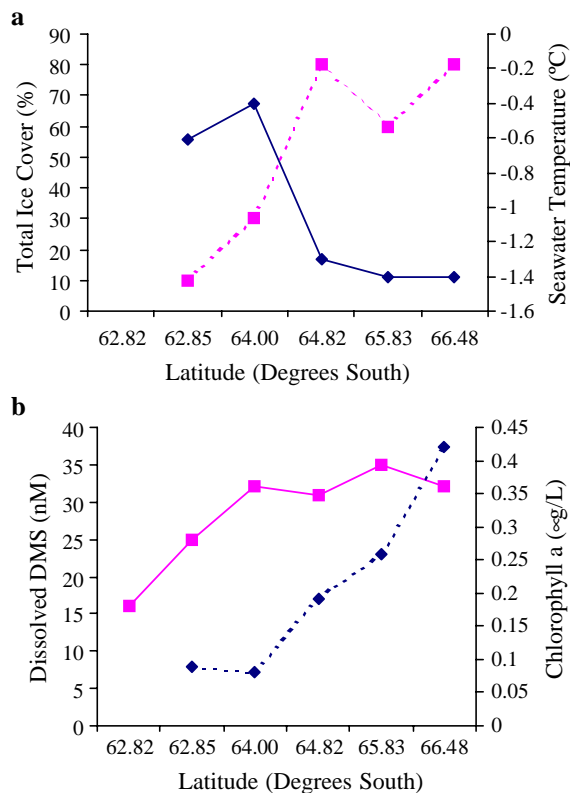Fig. 4. Sea ice depth and DMSPt or Chlorophyll-a concentrations for 2 rafted ice cores from site 13.

Fig. 5. (a) Total ice cover (%) (dotted line) and seawater temperature (continuous line) and (b) dissolved DMS (nM) (continuous line) and chlorophyll *a* (μg l⁻¹) (dotted line) at sample sites in the north–south V498 transect during mid-December 1998.

in the warmer waters (−0.4 to −0.6 °C) at the northern end of the transect. DMS concentrations ranged from 16 nM at 62.8°S to 35 nM at 65.8°S (means of triplicate measurements), with an overall average of 31 nM for the whole transect (*n* = 15). Chl *a* decreased from an average of 0.42 μg l⁻¹ at the southern most site, to 0.09 μg l⁻¹ at the northern most site.

In the Davis area on 22nd November (Table 4) DMSPd in under-ice seawater was 8 nM and DMSPp was not detected (i.e., DMSPd ≥ DMSP). At this time it appeared no melting of bottom ice had occurred, as the bottom algal assemblage showed luxuriant algal growth. A week later at a nearby site, DMSP concentrations had increased and melting of the bottom ice had begun, as the bottom algal assemblage appeared patchy with a more porous ice structure compared with the ice structure widely observed during spring. By early December the shallow interior fast ice was also melting, with the ice comprising a solid surface layer (about 0.3 m) and a 'slushy' deeper freeboard layer. Brine from the top 0.5 m was hyposaline (5 ppt), reflecting significant dilution from ice melting compared with the

Table 4
DMS(P) concentrations during fast ice melting in late November through December 2000 in the Davis area

Date	Sample	Salinity (ppt)	DMS(P) (nM)			Replicates
			DMSPp	DMSPd	DMS	
22 Nov	Under-ice seawater	37	nd	8	ns	1
28 Nov	Under-ice seawater	34	2	18	ns	1
7 Dec	Shallow ice brine	5	nd	149	ns	1
14 Dec	Surface melt pool	1 (1)	nd (nd)	7 (4–11)	1 (nd–1)	3
20 Dec	Tide crack seawater	4 (3–4)	nd (nd)	54 (52–56)	12 (11–12)	2
23 Dec	Surface seawater		61 (51–71)	16 (8–24)	10 (5–14)	2
6 Jan			29 (21–41)	11 (10–11)	2 (nd–2)	3
9 Jan			176 (170–186)	56 (44–75)	5 (nd–6)	3
14 Jan			130 (93–154)	69 (35–103)	2 (2–3)	3
19 Jan			289 (275–303)	45 (41–49)	2 (2–3)	3
20 Jan			59 (41–73)	36 (29–42)	3 (2–3)	3
25 Jan			100	20	1	1
2 Feb			48 (46–49)	10 (6–14)	1 (1)	3
13 Feb			71 (68–74)	24 (13–35)	3 (nd–3)	3
20 Feb			48 (39–53)	25 (10–35)	2 (2–3)	3

nd = not detected: for DMSPp = DMSPd ≥ DMSPt; for DMS = < 0.3 nM.
ns = not sampled.

typical hypersaline conditions of mid November (>70 ppt; Thomson, 2000). DMSPd in the brine was 149 nM while DMSPp was below detection. By mid December, melt pools of almost freshwater (1 ppt) were scattered across the fast ice surface. Though the ice cover was still intact, the upper half metre was very 'rotten', consisting of a brine/melt filled freeboard cavity covered by a porous surface layer (about 0.3 m). Below this freeboard cavity the deeper ice remained quite solid. In a surface melt pool, DMSP and DMS concentrations were very low (Table 4). By late December tide cracks at the coastal margin of the fast ice were 1 to 2 m wide and although the fast ice cover remained intact, it was almost completely decayed from the surface to the freeboard layer and there was probably little brine left in the very open ice structure (sampling not possible as too dangerous). Seawater salinity in a tide crack was 3 to 4 ppt, indicating the presence of a freshwater melt lens. In this tide crack, the average DMSPd concentration was 54 nM, DMSPp was not detected and DMS was 12 nM.

Concentrations of DMSPp, DMSPd and DMS in surface seawater from the Davis area, from late December 2000 through February 2001, are also given in Table 4. Following the break out of the fast ice cover on the 21st December during two days of winds >15 m s^{-1}, DMSP concentrations through to early January were relatively constant, ranging from 21–71 nM for DMSPp and 8–24 nM for DMSPd. DMS concentrations were highest two days after the fast ice cover broke out (up to 14 nM) and decreased to less than 6 nM through January and February.

Parallel increases in DMSP and DMS occurred over a ten day period from 9–19th January (Table 4). DMSPp concentrations dropped sharply on the 20th January (average 59 nM) to about one fifth of the previous day's average. The average DMSPd concentration also decreased, while DMS remained similar. Through late January and February, seawater DMSP and DMS concentrations remained relatively constant. Throughout this period the ratio of DMSPp:DMSPd also remained relatively constant (2 to 6) and their concentrations were significantly correlated ($r = 0.49$, Pearson, $P < 0.01$). Ratios of DMSP:DMS varied considerably (6–145 for DMSPp, 2–35 for DMSPd) and concentrations were not correlated (Pearson). However, the generally parallel profiles of DMSP and DMS concentrations imply that a relationship did exist between them.

4. Discussion

4.1. Relationship between DMSP and ice thickness

The larger DMSP concentration found in young ice may reflect higher biomass of ice algae and/or greater cellular DMSP concentrations in the newly incorporated sea ice algae. Newly incorporated ice algae are exposed to higher light levels in young ice compared with algae in mixed layer seawater and, as light is an important factor influencing both productivity in polar oceans (e.g., Lancelot et al., 1993) and DMSP synthesis (Karsten et al., 1992), it may encourage greater cellular DMSP. DiTullio et al. (1998) reported that an algal

community recently incorporated from the seawater into grease ice (unconsolidated ice crystals) had 1 fmol DMSP cell^{-1}, while communities from young ice had substantially larger cellular DMSP (46 and 103 fmol cell^{-1}), similar to concentrations in a rafted ice community (40 fmol cell^{-1}). These authors found that the increasing cellular DMSP in the different ice thicknesses could not be explained by differences in the taxonomic composition of the communities, with regard to *Phaeocystis* sp. (considered to be a high DMSP producing alga), as *Phaeocystis* sp. made up 97% of cell numbers in the grease ice community and less than 20% in the older ice communities, while diatoms comprised the remaining majority. Cellular DMSP in Antarctic ice algae however appears to be variable, with Kirst et al. (1991) reporting DMSP concentrations ranging from 60–420 fmol DMSP cell^{-1} for algal communities dominated by diatoms (90%). In Arctic sea ice, Levasseur et al., 1994 reported that diatoms from a bottom fast ice community had DMSP concentrations of 9 fmol cell^{-1}.

The exponential relationship between DMSP concentration and ice thickness reported here is likely applicable only for consolidated ice sheets with a minimum thickness of young ice (0.1 m) and not for unconsolidated areas of grease ice nor for platelet ice. Young ice in our data set is represented by 3 cores collected from a single site (site 12; Table 1) and it is possible that the greater DMSP concentrations in this category reflect the influence of local conditions and are not representative of this ice thickness. For example, compared with DMSP concentrations for sections of young ice reported by DiTullio et al. (1998) from 3 sites in the Ross Sea (5–980 nM, average 232 nM), concentrations from sections of our eastern Antarctic young ice were greater (187–1730 nM, average 480 nM). However, DMSP concentrations in sections of our first stage thin ice (81–763 nM, average 301 nM), collected from three sites (sites 2, 5, 13; Table 1), were similar to concentrations reported by Curran and Jones (2000) from 5 sites in the same region, Prydz Bay (22–700 nM, average 171 nM). Considering the variability of DMSP in sea ice, a larger data set of DMSP concentrations in thinner ice (<0.3 m) is required to establish whether they are characteristically much greater than in thicker ice. Currently, the data set of sea ice DMSP concentrations is predominantly comprised of ice greater than around 0.5 m thick.

Seasonal constraints also are likely to apply to our exponential relationship between DMSP and ice thickness, such that it should not be considered applicable for autumn/winter sea ice until appropriate DMSP data

sets are obtained during these seasons. There is some evidence that sea ice DMSP concentrations show a seasonal cycle of winter minima and spring/summer maxima, which parallels sea ice productivity. Curran et al. (1998) reported an average winter sea ice DMSP concentration of 40 nM, which was significantly lower than their spring average (144 nM). However, their winter and spring sea ice were collected from different regions (140°E and 75°E, respectively) between which differences in biological and physico-chemical properties may have influenced the difference in DMSP (Curran et al., 1998). A similar average winter concentration of 25 nM was found in sea ice from the Mertz Glacier polynya (around 147°E; Jones and Mercurio, unpublished). Even during the spring/summer, it is possible that seasonal changes in DMSP affect its apparent relationship with ice thickness. We did not find evidence of a seasonal progression in our sea ice DMSP data for the 2 six week spring/summer sampling periods (data not shown). However, our sample sites were spread over a large area of the ASIZ and any influence from seasonal change would probably be difficult to elucidate against the known high spatial variability in sea ice DMSP (Kirst et al., 1991; Turner et al., 1995; Curran et al., 1998; DiTullio et al., 1998; Trevena et al., 2000, 2003; Gambaro et al., 2004), biomass and taxonomic composition (e.g., Ackley and Sullivan, 1994) and physico-chemical properties (e.g., structure (Worby et al., 1998), bulk salinity (Trevena et al., 2000, 2003) and nutrients (Gleitz et al., 1995; Trevena et al., 2000, 2003).

4.2. Release of DMS(P) from sea ice during ice melting

The very low DMSPp concentrations in under-ice seawater (Table 4) are similar to the average reported by Kirst et al. (1991; 3 nM) from seawater under Weddell Sea pack ice, also during late spring. DMSPd concentrations are similar to those reported by Gibson et al. (1990; approximately 0–10 nM) and McTaggart and McTaggart and Burton (1992; approximately 413 nM) for under-ice seawater in the Davis area during spring. The decrease in under-ice seawater salinity during late November likely reflects an increase in the drainage of low salinity brine from the overlying ice as the shallow interior ice melted, a process that transports dissolved and particulate material from the ice to the under-ice seawater. The associated increase in DMSPd suggests that the under-ice DMSP was derived mostly from the overlying fast ice. It is also possible that the DMSPd may have been derived from the senescent phase of a sub-fast ice *Phaeocystis* sp. bloom. These sub-ice blooms have been reported

to occur in the Davis area during November–December (McMinn, 1996) and were concluded to be responsible for elevated DMSP in under-fast ice seawater in Terra Nova Bay during December (Gambaro et al., 2004). However, it is also possible that some of the total DMSP (DMSPp+DMSPd) Gambaro et al. (2004) found was released from the overlying fast ice, which was presumably melting at that time.

Assuming the under-ice seawater DMSP was mostly derived from the melting fast ice, DMSP release from the ice appeared to be almost all as extracellular DMSP, based on the dominance of DMSPd in the under-ice seawater and shallow interior brine (Table 4). The transformation of DMSPp to DMSPd in fast ice brine may have occurred in response to changing salinity, as brine in shallow interior fast ice decreases from hypersaline levels (>70 ppt) in mid-November to hyposaline (<20 ppt) by mid-December (Thomson, 2000). Considering that DMSP functions as an osmolyte in some marine algae (Dickson and Kirst, 1986), it is probable that in response to the rapidly decreasing osmotic conditions ice algae would release some DMSPd. In addition, the release of DMSPd following cell death may have contributed to the dominance of extracellular DMSP, as it has been reported that mortality amongst interior fast ice algae is high (Archer et al., 1996; McMinn, 1996; Thomson, 2000) and grazing activity increases during ice melting with the widening of brine channels (Archer et al., 1996; Thomson, 2000). The transformation of DMSPp to DMSPd via micro-zooplankton grazing was reported to be approximately 10% to 20% day^{-1} in experiments using seawater from high northern latitudes (Archer et al., 2001). In ice melting incubation experiments in Antarctic waters, DMS production increased in the presence of juvenile krill (Daly and DiTullio, 1993). In addition, grazing may influence the fate of sea ice DMSP through transportation, as grazers apparently consume a large proportion of ice algae released during melting (Lancelot et al., 1993; McMinn, 1996; Wright and van den Enden, 2000). This grazing during ice melting may facilitate transport of sea ice DMSPp to deeper waters through the production of fast sinking faecal pellets during grazing in the lower salinity surface waters, in a similar fashion to DMS(P) dynamics in estuaries (Tang, 2000).

DMSP in brine during early December was less than concentrations reported by Thomson (2000; range 239–451 nM) from the same Davis area during November to December 1997. However, it was greater than the average concentration of 62 nM in pack ice brine reported by Kirst et al. (1991), although these authors considered this value conspicuously low compared with other sea

ice assemblages (average 322 nM). It appears that brine DMSP shows high variability similar to that found in bulk sea ice DMSP.

In the surface melt-pool, DMSPd was low compared with DMSP in fast ice surface assemblages from the Davis area during spring (average 79 nM; Trevena et al., 2003). Salinity in the melt-pool was at least fivefold less than the average bulk salinity of surface and upper interior fast ice from the same area (5 and 7 ppt, respectively; Trevena et al., 2003) and this dilution probably accounted, in part, for the lower DMSPd. Although interior ice algae are able to survive a wide range of salinities from hyper- to hyposaline (Thomson, 2000), it seems unlikely that they would show active growth in the almost fresh melt-pool. Considering this, and the low concentrations of DMSPd and DMS, it appears that in fast ice surface melt-pools any in situ production of DMS(P) was negligible.

In a tide crack in late December, the average concentration of DMSPd was about five times greater than in under-ice seawater one month previously (Table 4). DMSPd in the tide crack represented around 55–60% of the average DMSP concentration in surface and shallow interior fast ice assemblages from the Davis area (see above). Whilst highly speculative the deficit in DMSPd between these habitats may have been due to bacterial consumption in the tide crack, as biological activity there was likely to have been high due to the meltwater lens producing a shallow mixed layer (Lancelot et al., 1993; Wright and van den Enden, 2000), as well as high light levels compared with under-ice seawater. DMSPd consumption by bacteria can occur via a number of pathways including: enzyme cleavage to produce DMS (Kiene and Service, 1991; Visscher et al., 1992; Ledyard and Dacey, 1996) and demethylation to produce 3-mercapto propionate (MPA) or methanethiol (MeSH) (Visscher et al., 1992; Kiene and Linn, 2000). DMS concentrations in the tide crack represented 12–14% of DMSP in surface and shallow interior fast ice assemblages.

The percentage DMS concentration in surface melt water lens's in both fast and pack ice areas relative to that of sea ice DMSP suggests 10–25% of sea ice DMSP may be converted to seawater DMS during ice melting. This range is similar to percentages reported for other marine environments: 9% (MeSH+DMS; Kiene and Linn, 2000); 15% (Ledyard and Dacey, 1996); and <30% (Kiene and Service, 1991). However, the fraction of DMS produced from DMSP degradation appears to be a dynamic quantity influenced by physico-chemical conditions with DMS production at times being the major fate of DMSP degradation. For exam-

ple, in very shallow mixed layers in the North Atlantic (60°N) Simó and Pedrós-Alió (1999) reported that close to 100% of DMSP was converted to DMS. These authors suggested that vertical mixing controlled the efficiency of DMSP conversion to DMS via a number of biological and physical effects including a higher DMSP turnover in shallow mixed layers via increased bacterial activity. During sea ice melting, such shallow mixed layers develop due to vertical stability of the water column through the input of low salinity melt water (Lancelot et al., 1993). The fraction of DMS produced from DMSPd degradation also reportedly increases under conditions of either decreasing temperature (25 °C c.f. 7 °C) or increasing DMSPd concentration (3% at 0.5 nM to 22% at 20.5 nM; Kiene and Linn, 2000). In the ASIZ during ice melting, seawater temperatures may be less than 0 °C (i.e., Fig. 5a) and seawater DMSP concentrations are likely to be elevated, based on concentrations of seawater DMS and sea ice DMSP. Therefore, in the ASIZ during sea ice melting, physico-chemical conditions may at times favour DMS production as a major fate of sea ice DMSP degradation (i.e., >30% DMS from DMSPd).

4.3. DMS released at the retreating pack ice edge

At the retreating pack ice edge during mid December, the elevated DMS concentrations in surface seawater (average=31 nM) agree with the findings of Kirst et al. (1993), that during the period of ice melting DMS production in the ASIZ may be particularly large. The extremely high dissolved DMS concentrations from our V498 transect appear to have been associated with the release of DMS and DMSP from the melting pack ice and not from in situ production by an ice edge bloom. Chl *a* concentrations at the ice edge (63–64°S) were relatively low (<0.1 µg l^{-1}; Fig. 5), suggesting an ice edge bloom had not developed (for bloom conditions Chl *a* >1.5 µg l^{-1}; Tréguer and Jacques, 1992). From about 63°S to 66.5°S DMS concentrations averaged 25–35 nM, and these dissolved DMS concentrations were nearly threefold greater than the average sea ice DMS concentrations (12 nM) found in open water. This difference suggests that in the 63–66.5°S latitudinal band dissolved DMS was derived primarily from sea ice DMS and DMSP, released during ice melting. In September 1994 slightly elevated concentrations of atmospheric DMS were measured above the sea ice in the 62–63°S latitudinal band (75–100°E), where the highest concentrations of DMSP occurred in the sea ice (Curran and Jones, 2000). The DMS concentration in surface seawater at the retreating ice edge

(63–66.5°S) was 8% of the total DMSP concentration reported for the eastern Antarctic pack ice (380 nM; Trevena et al., 2000) and suggest that dissolved DMS concentrations may be even higher than reported here. The oxidation of dimethylsulphide (DMS) to acidic aerosols influences aerosol nucleation, growth and cloud albedo, affecting the radiative climate, and is important over unpolluted environments such as the ASIZ, where DMS-derived compounds are most probably a significant proportion of the aerosol (Leck et al., 2004). We have recently reported satellite-derived chlorophyll-a (CHL) and aerosol optical depth (AOD) time series between 50–70°S over the Southern Ocean and the ASIZ (Gabric et al., 2005). We find strong coherence in CHL and AOD signals in the ice-free zone (50–60°S), suggesting a close coupling between phytoplankton, DMS dynamics and aerosol load. However, this synchrony is absent over the ASIZ (60–70°S) where the AOD peak in spring often precedes the main summer CHL peak by up to six weeks. We believe this is due to large pulses of DMS emanating from melting sea ice (Jones, Trevena and Gabric, in prep.).

4.4. DMS and DMSP in seawater during summer

Concentrations of DMSPp and DMSPd reported in Antarctic surface waters during November to February are summarised in Table 2. The range of DMSPd concentrations we found in the Davis area are similar to those reported by Gibson et al. (1990; 1–100) during December 1987 but our average (32 nM) is substantially less than the averages reported by McTaggart and Burton (1992) for December 1988 and January 1989 (95 and 214 nM, respectively). These later authors attributed the high DMSPd concentrations to high primary productivity (average Chl *a* approximately 20 µg l^{-1}). During the ice-free summer in the coastal Davis area, average DMSPd concentrations (>30 nM) are much higher than those in open ocean waters (<15 nM). Similarly, our average concentration of DMSPp was also higher than in open ocean waters (<30 nM). However in other coastal areas, lower DMSP concentrations have been reported during the ice-free summer (<10 nM; DiTullio and Smith, 1993; Gambaro et al., 2004). These low concentrations were associated, respectively, with low phytoplankton biomass (average 0.15 µg l^{-1}) during November and a bloom of low DMSP producing phytoplankton during February. The apparently higher seawater DMSP in the Davis area may be associated with typically greater summer productivity or a community composition

with a greater portion of higher DMSP producing phytoplankton, or it may simply be coincidental sampling at times of elevated DMSP, as we know that concentrations show high spatial and temporal variability in the ASIZ (i.e., Table 2).

Concentrations of DMS reported in Antarctic surface waters (up to 62°S north) during November to January are also summarised in Table 2. Average concentrations for individual studies range over two orders of magnitude, from approximately 1 to 100 nM. Prior to the beginning of sea ice melting during October and November, seawater DMS concentrations appear to be typically less than 10 nM (DiTullio and Smith, 1993; McTaggart and Burton, 1992; Turner et al., 1995), which is generally similar to concentrations reported from other ocean regions (e.g., Kettle et al., 1999). During the period of sea ice melting (December through January), concentrations appear to be generally higher (up to 100 nM). Our average DMS concentration for the V498 transect is similar to averages > 20 nM from four other studies. During late December through mid February in the Davis area, DMS concentrations were at the low end of ranges reported for Antarctic surface waters (ca < 1–100 nM). Note that the relatively large DMS concentrations reported from early Davis area studies may have been overestimated, as they used mercuric chloride for sample preservation and this treatment may have converted some DMSP to DMS (Turner et al., 1995; Curran, 1997). Elevated DMS concentrations, greater than approximately 50 nM, have generally been associated with *Phaeocystis* sp. dominated biomass in ice-free waters (Gibson et al., 1990; Kirst et al., 1993; McTaggart and Burton, 1992; Crocker et al., 1995; DiTullio and Smith, 1995; DiTullio, 1996).

Between the 19th and 20th January, the dramatic decrease in DMSPp (Table 4) may have been due, in part, to dilution following a light overnight snowfall and very calm wind conditions. It may also have been influenced by a short-term increase in grazing pressure due to the presence of a krill species (approximately 5–10 mm in length) that was abundant on the 20th January (2–10 individuals collected in each sampling bucket cast). It is possible that through increased grazing a substantial amount of DMSPp was transported out of the surface waters via fast sinking faecal pellets (as discussed previously) or with migration of the grazers. Support for this grazer mediated transport process to remove DMSPp comes from the fact that only small increases in DMSPd and DMS concentrations were

observed. This suggests that transformation and degradation processes, to produce DMSPd and DMS, were not primarily responsible for the DMSPp removal.

Ratios of seawater DMSPp : DMS and DMSPd : DMS in the Davis area during late December through mid February varied considerably, with averages of 48 and 14, respectively. These averages are substantially larger than the ratio of 7 found for DMSP : DMS in Southern Ocean surface waters (Curran, 1997). The range of DMSPd : DMS ratios during the summer varied from 1.6 immediately following the fast ice break out to 30 during mid January (data not shown). This variation may reflect that the production and turnover of DMSP and DMS were dynamic during the ice-free summer period. Kinetic parameters of DMSP turnover and DMS production have been reported to vary seasonally (Ledyard and Dacey, 1996), possibly associated with changes in composition of the bacterial community (Visscher et al., 1992). As phytoplankton blooms in the Davis area show a seasonal succession during the ice-free summer (e.g., McMinn and Hodgson, 1993; Gibson et al., 1990), it is possible that the bacterial community may also show similar seasonal succession. If so, the dynamics of DMS(P) turnover and production in ice-free Antarctic waters may also follow a seasonal pattern.

5. Conclusions

The first measurements of dissolved DMS have been reported for sea ice from eastern Antarctica and ranged from < 0.3 to 75 nM with an average concentration of 12 nM. The average concentration of DMSP in young ice from eastern Antarctica was 480 nM. DMSP was significantly greater in young ice, than medium and thick ice, but not thin ice. In rafted ice floes however, DMSP concentrations were the highest encountered. This suggests that in most cases the greatest concentration of DMSP occurs in recently formed sea ice. This suggests that the ASIZ is a huge reservoir of DMS and DMSP to the surrounding seawater when sea ice melts. DMSP varied exponentially with sea ice thickness and the derived equation suggests that DMSP "hot spots" could be detected in the Antarctic sea ice if good records of sea ice thickness can be obtained. During a 500 km transect through the eastern Antarctic sea ice zone in December extremely high concentrations of dissolved DMS were measured (31 nM) with the bulk of these measurements coinciding with low chl a concentrations. This could suggest that large amounts of DMS are released from melting sea ice and are not

necessarily produced from in situ production of chl a. Further studies are needed to confirm this.

Acknowledgments

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