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Elevated levels of dimethylated-sulfur compounds in Lake Bonney, a poorly ventilated Antarctic lake

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Abstract

Lake Bonney is a permanently ice-covered lake in the McMurdo Dry Valleys, Antarctica. The lake has two chemically stratified lobes (referred to as the east and west lobes), each with distinct biogenic sulfur profiles. Dimethylsulfoniopropionate ($DMSP_p$) and dimethylsulfoxide ($DMSO_p$) exceeded 32 and 2 nmol L^{-1}, respectively, in the photic surface waters of the lake. Maximum $DMSP_p$ levels occurred in the deep-chlorophyll layer of both lobes, a zone dominated by chrysophytes and chlorophytes, which are thought to be the source of dimethylated sulfur in the deep waters of the lake following sedimentation and biogeochemical processing. Waters beneath the chemoclines of both lobes are cold (<0°C), saline (>3 times seawater), suboxic, and devoid of phytoplankton biomass and activity. Dimethylsulfide (DMS) levels (>330 nmol L^{-1}) in the deep west lobe are among the highest recorded in a natural aquatic ecosystem. In contrast, saline waters of the deep east lobe contain relatively little DMS (<70 nmol L^{-1}) but high $DMSO_d$ (270 nmol L^{-1}), with the latter being the highest observed in any natural aquatic ecosystem. We argue that the differences in the biogenic sulfur profiles between the deep waters of the two lobes arise principally from subtle differences in the redox conditions found in each lobe.

The cycling of the biogenic gas dimethylsulfide (DMS), along with that of the closely related compounds dimethylsulfoniopropionate (DMSP) and dimethylsulfoxide (DMSO), has received considerable attention because of the significant role DMS plays in modifying planetary climate (Charlson et al. 1987). Most research activity has focused on oceanic environments, since DMS is the most abundant volatile sulfur compound in the world's oceans (Malin et al. 1992; Liss et al. 1997). The biogeochemical cycle of these compounds in seawater is complex. Both DMSP and DMSO are present in phytoplankton (Vairavamurthy et al. 1985; Simó et al. 1998*a*), but production of each compound appears to be strongly species dependent (Keller et al. 1989; Lee et al. 2001). Release of intracellular DMSP and conversion to DMS occurs through a number of processes including grazing, viral infections, the lysis of senescent cells, and enzymatic cleavage (*see* reviews by Malin et al. 1992; Liss et al. 1997; Simó 2001). DMS can be removed through sea–air exchange, microbial transformation, and photo-oxidation (*see* reviews by Malin et al. 1992; Liss et al. 1997; Simó 2001). The factors influencing DMSO concentrations are less well understood but are thought to involve some of the same processes outlined above for DMSP and DMS (Lee and de Mora 1999; Lee et al. 1999; Simó et al. 2000).

Unlike oceanic environments, current knowledge of these three compounds in freshwater ecosystems is limited (Simó et al. 1993; Lee et al. 1999). Despite this shortcoming, research on small, intense continental sources of dimethylated

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sulfur, in particular DMSP and DMS, has helped to elucidate the ecological importance and role of these compounds and to delineate biogeochemical linkages between them. Studies on melt-water ponds in Antarctica and continental lakes in the Mediterranean region have shown that cyanobacteria, cryptomonads, and freshwater dinoflagellates can be important producers of DMSP (Simó et al. 1993; de Mora et al. 1996; Ginzburg et al. 1998), despite evidence to the contrary from culture experiments (Keller et al. 1989). Results from several lakes on the Canadian Shield have revealed a strong correlation between DMSP and sulfate concentrations (Richards et al. 1994). Methanogenesis has been shown to be an important loss mechanism for both DMS and DMSP in Mono Lake, California (Visscher et al. 1996). Findings from Organic Lake, Antarctica, indicate that organic polysulfides, such as dimethyldisulfide and dimethyltrisulfide, can be precursors to DMS rather than DMSP (Roberts et al. 1993).

Lake Bonney in the McMurdo Dry Valleys, Antarctica, is covered by an approximately 4-m thick layer of perennial ice that causes unusual ecosystem properties. Less than 5% of the sunlight that reaches the lake's surface penetrates to the water column, and photosynthetic activity is restricted to a 6-month period centered on the austral summer, when sufficient sunlight is available. As a consequence, ratios of annual net production to respiration are less than one (Priscu et al. 1999). Metazoan grazers are virtually absent in the plankton community, with protozoans being the highest trophic level present (Priscu 1997; Priscu et al. 1999). The permanent ice-cover and low stream inflow produces water columns in which vertical transport is dominated by molecular diffusion (Spigel and Priscu 1998). Atmospheric exchange of dissolved gases is reduced, producing surface waters that are supersaturated with gases including oxygen and nitrous oxide (Craig et al. 1992; Priscu 1997). During past research efforts at Lake Bonney, the distinct smell of DMS could be consistently detected in the lower layer of the west lobe of the lake. This zone of Lake Bonney is aphotic and devoid of phytoplankton biomass and activity (Lizotte et al. 1996). Subsequent measurements have revealed that DMS levels were as high as those associated with intense phytoplankton blooms in oceanic environments. Furthermore, maximum concentrations of particulate DMSP occurred in the deep chlorophyll layer, a zone dominated by chrysophytes and chlorophytes (Lizotte and Priscu 1998), which are not normally considered significant DMSP producers (Keller et al. 1989). The purpose of this study was to make detailed measurements of DMS, DMSP, and DMSO and to examine the biogeochemical cycling of DMS and these compounds in Lake Bonney.

Methods

Sample site—Lake Bonney (77°43′S, 162°20′E) lies at the western end of the Taylor Valley, one of the McMurdo Dry Valleys in southern Victoria Land, Antarctica (Priscu 1997). The lake is divided into two lobes (east and west) by a sill at a depth of 12–13 m, with each lobe having a maximum depth of 40 m. Each lobe is further divided vertically into two layers by a chemocline at a depth of approximately 20 m in the east lobe and 15 m in the west lobe. An oxycline also occurs at the same depths, with suboxic conditions occurring beneath the oxycline (Lee et al. 2004). Temperatures in the bottom layers reach lows of approximately −2°C and −5°C in the east and west lobes, respectively, with conductivities three to five times that of seawater (Spigel and Priscu 1998).

Sample collection and preparation—Samples were collected in November and December 1999 and again in November and December 2000. Sampling was conducted at locations that corresponded to the deepest parts of each lobe and coincided with the sampling program for the McMurdo Long Term Ecological Research (LTER) limnology program. Water samples were collected with a 5-liter Niskin bottle and transferred to sample bottles with silicon rubber tubing. Subsamples for the analysis of DMS were transferred (unfiltered) to 125-ml Wheaton serum bottles, filled to capacity to eliminate any headspace, and sealed with butyl rubber stoppers and aluminum crimp seals. Subsamples for the analysis of DMSP and DMSO, high-performance liquid chromatograph (HPLC) pigments, chlorophyll *a* (Chl *a*) by fluorometry, nutrients, and acrylic acid were transferred to 1-liter amber high density polyethylene (HDPE) bottles for return to the field laboratory for subsequent processing (within 2 h of collection). Subsamples for the enumeration and identification of phytoplankton by microscopy were transferred to 500-ml amber HDPE bottles, preserved with 10 ml acid Lugol's solution, and stored for several months in the dark at 4°C until analyzed (American Public Health Association 1985).

Upon return to the field laboratory, 200-ml aliquots of the sample were filtered through Whatman GF/F filters for particulate DMSP and DMSO samples. A small amount of vacuum (<100 mm Hg) was applied to the samples to assist the filtration procedure. The filter for $DMSP_p$ was placed in a 20-ml serum vial along with 5 ml HPLC-grade methanol and capped with butyl rubber stoppers and aluminum crimp seals. The same procedure was followed for the filters for $DMSO_p$, except that 5 ml of 6 mol L^{-1} HCl was used as the preservative instead of methanol. The volume of sample filtered for $DMSO_p$ was increased from 200 ml to 1 liter when it became apparent that a larger volume was required to successfully measure DMSO in the particulate phase. Sixty-milliliter aliquots of the filtrate from the particulate sample preparation were collected for the $DMSP_d$ and $DMSO_d$ samples. The dissolved-phase samples were placed in 60-ml serum bottles, preserved with 1 ml methanol (for $DMSP_d$) or 1 ml of 6 mol L^{-1} HCl (for $DMSO_d$) and sealed as per the DMS samples.

Analysis of dimethylated-sulfur compounds—DMS concentrations were determined using a cryogenic purge-and-trap technique (DiTullio and Smith 1995) on samples prepared immediately at the time of collection. DMS and $DMSP_d$ samples were analyzed within 8 and 24 h, respectively, of sample collection. All other samples for dimethylated sulfur were stored for later analysis (within 4 months of collection). Instrumental analysis of DMS was carried out using either a Varian Star 3400CX gas chromatograph or a

Hewlett-Packard 5890 Series II gas chromatograph equipped with a flame photometric detector. The Varian instrument was fitted with a Teflon column containing Carbopack B/1.5% XE60/1% H_3PO_4 (Supelco), and temperature programming (40–140°C) was used to achieve baseline separation of DMS and carbon disulfide (de Mora et al. 1996). The Hewlett-Packard instrument was set to isothermal conditions (70°C) and fitted with a Chromosil 330 column (Supelco; DiTullio and Smith 1995). Calibration of the instruments was achieved using permeation devices (DiTullio and Smith 1995; de Mora et al. 1996). The detection limit for DMS was 0.03 nmol L^{-1}, with coefficients of variation of 11% on the Varian instrument and 9% on the Hewlett-Packard instrument. The analytical procedure used for DMS could also be used to determine methanethiol levels. The detection limit for methanethiol was 0.02 nmol L^{-1}, with a coefficient of variation of 8% on the Hewlett-Packard instrument.

$DMSP_d$ and $DMSP_p$ samples were hydrolyzed in strong alkali (1 mol L^{-1} NaOH) and measured as DMS. All DMSO samples were analyzed using the sodium borohydride reduction method (Simó et al. 1998*b*). $DMSO_2$ (dimethylsulfone) was analyzed according to the methodology of de Mora et al. (1996). This procedure involved fitting the Varian gas chromatograph with a Teflon column containing 15% Free Fatty Acid Phase on 40-60-mesh Chromosorb T and injecting the samples directly into the chromatograph via a heated on-column injector port. The instrument was also fitted with flow controllers to allow introduction of sulfur hexafluoride (SF_6) to improve flame sensitivity. The detection limit of the Varian instrument for $DMSO_2$ was 18 nmol L^{-1}, with a coefficient of variation of 10%.

Chl a, *ancillary data, and acrylate*—Chl *a* samples were filtered onto Whatman GF/F filters. The filtrate was collected in a 125-ml HDPE bottle and frozen for subsequent nutrient analysis. The GF/F filters were folded in half with the organic matter on the inside of the fold and placed in glassine envelopes, which were then wrapped in aluminum foil and frozen for 2–3 weeks until the samples could be analyzed. Upon analysis, the samples were extracted in 1 : 1 DMSO : 90% acetone for 12 h under cold (−20°C), dark conditions. Final determination of the Chl *a* was by fluorometry (Dore and Priscu 2001).

The ancillary data (temperature, salinity, pH, particulate organic carbon, particulate organic nitrogen, nitrate, nitrite, and ammonium) were collected as part of the LTER limnology program (Priscu et al. unpubl. data). Full details regarding the methodology used to collect this data can be found elsewhere (Priscu 1997; Dore and Priscu 2001).

A 20-ml aliquot of the filtrate from the preparation of $DMSP_p$ samples was placed in a 20-ml serum vial, sealed, and stored for the determination of acrylate (within 2–3 weeks of sample collection). Measurements for acrylate were carried out following the methodology of Gibson et al. (1996) using a Hewlett-Packard HP1050 HPLC system equipped with a diode array detector set to 210 nm. The eluent was 0.1% H_3PO_4 delivered at a flow rate of 1 ml min^{-1}. The limit of detection for acrylate was 3 nmol L^{-1} using a 100-μl sample injection volume.

Phytoplankton identification and enumeration—The samples preserved in Lugol's were gently mixed, and 100 ml was settled in 100-ml graduated cylinders and subsequently transferred to 20-ml Utermöhl chambers to further concentrate the sample (Utermöhl 1957). Preliminary experiments with samples from Lake Bonney revealed that, in a 100-ml graduated cylinder, 100-ml aliquots of samples from 18 m took 120 h for complete sedimentation to occur. After each sample had settled for 120 h, the supernatant water was siphoned off using a pipette with a curved tip attached to a vacuum pump until 20 ml of the settled sample remained in the bottom of the graduated cylinder. The 20-ml sample was gently mixed and settled a second time in a 20-ml Utermöhl chamber for an additional 24 h.

A Nikon Diaphot inverted microscope with phase contrast was used to identify and enumerate the phytoplankton species. Identification of phytoplankton cells was made at ×1,000 magnification and based on the keys of Seaburg et al. (1979), Prescott (1978), and Whitford and Schumacher (1984). All phytoplankton cells were identified to at least the genus level. The phytoplankton species were enumerated at ×400 magnification. Approximately 300 individual cells of the dominant species were counted in each sample and expressed as cells per milliliter in the original sample. This protocol yielded a counting error of approximately 12% (Lund et al. 1958). Biovolume was estimated from the average geometric shapes of at least 10 individuals of each genus (Hillebrand et al. 1999).

HPLC pigments—Samples were collected for the measurement of chlorophyll and carotenoid concentrations (collectively referred to as pigments) by HPLC. Aliquots (0.5 to 2.0 liter) of lake water were filtered onto Whatman GF/F filters, which were immediately frozen and stored in liquid nitrogen until analysis (within 6 months of sample collection). Algal pigment samples were extracted in 90% acetone and analyzed using a gradient elution method (Zapata et al. 2000). The samples were analyzed using a Hewlett-Packard 1050 HPLC equipped with photodiode array and fluorescence detectors. Pigment standards were purified from algal cultures. The coefficient of variability of replicate injections of various standards was <3%.

Chloroform-inhibition experiments—Several experiments were conducted using chloroform inhibition to examine the production of DMS from the enzymatic hydrolysis of DMSP (Kiene and Service 1991). Water samples for the inhibitor experiments were collected from 13 m and 35 m in 1-liter HDPE bottles at the same time as the samples for the general survey and were returned to the lab for preparation. A surficial (upper ~3 cm) sediment sample was collected using an Ekman grab sampler and was taken to the lab for preparation. Aliquots (100 ml) of the samples were transferred to 125-ml serum bottles, and chloroform was added to treatment vials to ensure a final concentration of 500 μmol L^{-1}. In the case of the sediment samples, a 100-ml aliquot of the homogenized sediment slurry, which contained ~55% v/v water, was transferred to the serum bottles. The serum bottles (two unaltered controls and two chloroform-amended treatments) were sealed, as for the dimethylated-sulfur samples,

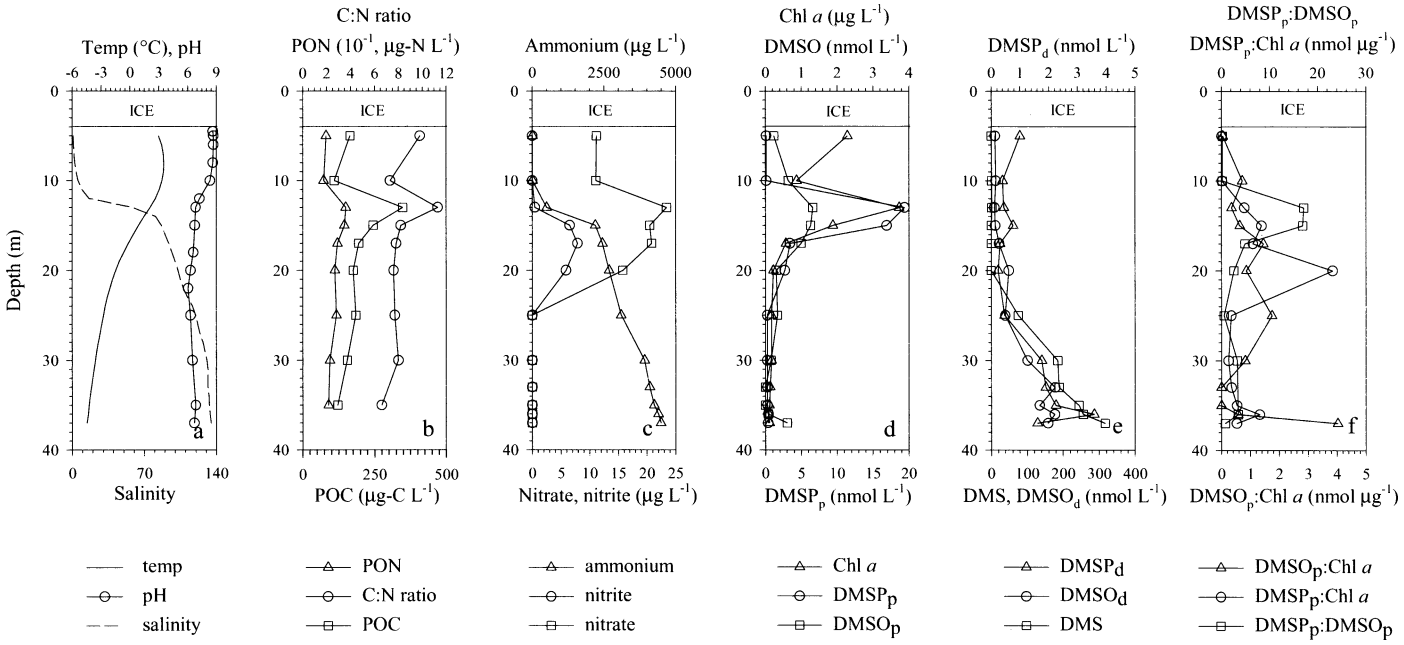

Fig. 1. Depth profiles from the west lobe of Lake Bonney for various physical and chemical parameters: a) temperature, salinity, and pH, b) nitrate, nitrite, and ammonium, c) particulate organic carbon, particulate organic nitrogen, and C : N ratio, d) Chl *a*, $DMSP_p$, and $DMSO_p$, e) $DMSP_d$, DMS, and $DMSO_d$, f) $DMSP_p$: Chl *a*, $DMSO_p$: Chl *a*, and $DMSP_p$: $DMSO_p$.

and incubated in the dark at 4°C. Initial experiments were run for a maximum of 16 h with a set of samples being analyzed every 1–3 h. For the sediment samples, the total sample (sediment + water) was analyzed for DMS. A second set of experiments was incubated for 5 d to allow a greater period of time for the reaction to occur. Time zero was taken as the time that the chloroform was added.

Results

Ancillary data, Chl a, *and acrylate*—Vertical profiles of temperature, salinity, pH, and nutrients reveal the strong vertical stratification that exists in both the east and west lobes of Lake Bonney (Figs. 1a–c and 2a–c, respectively). As indicated by other studies (e.g., Spigel and Priscu 1998), the

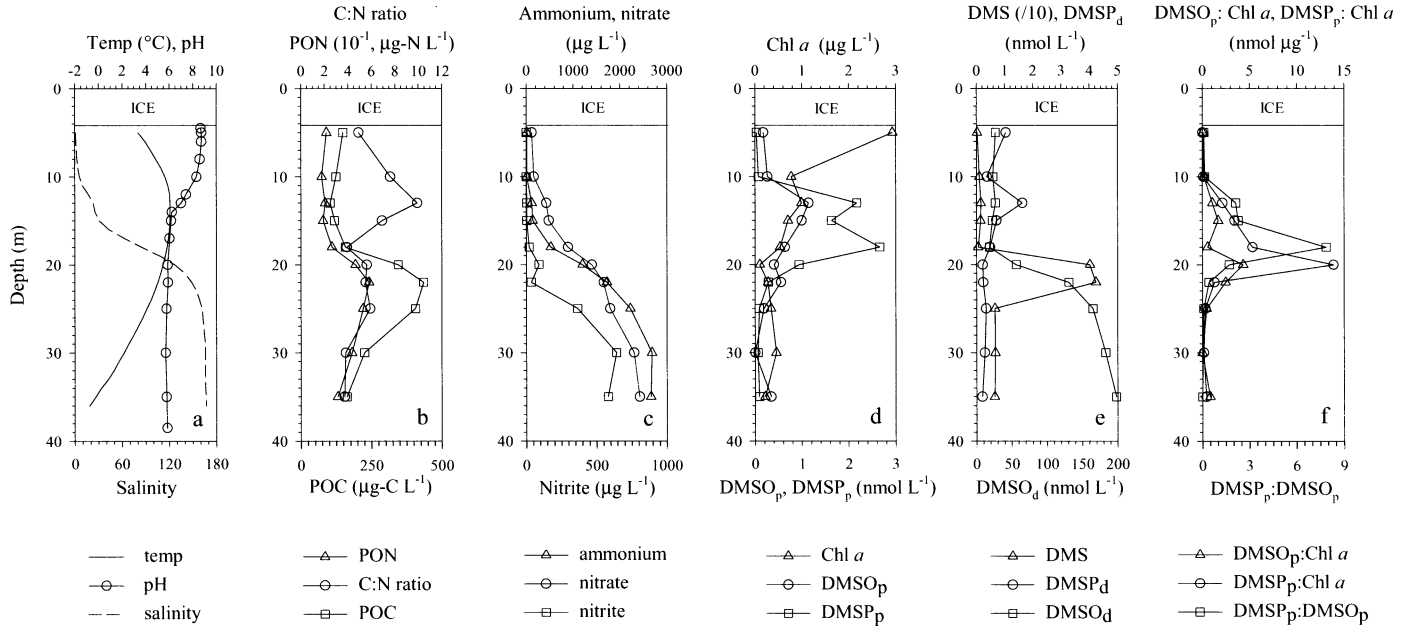

Fig. 2. Depth profiles from the east lobe of Lake Bonney of various physical and chemical parameters, a) temperature, salinity, and pH, b) nitrate, nitrite, and ammonium, c) particulate organic carbon, particulate organic nitrogen, and C : N ratio, d) Chl *a*, $DMSP_p$, and $DMSO_p$, e) $DMSP_d$, DMS, and $DMSO_d$, f) $DMSP_p$: Chl *a*, $DMSO_p$: Chl *a*, and $DMSP_p$: $DMSO_p$.

Table 1. Mean, median, range, and standard deviation (SD) for Chl *a*, particulate DMSP ($DMSP_p$) particulate DMSO, dissolved DMSP, DMS, and dissolved DMSO for selected depth intervals in the west lobe of Lake Bonney. The summarized data are from samples collected during the austral summers of 1999–2000 and 2000–2001.

Variable	*n*	Mean	Medium	Minimum	Maximum	SD
Chl *a* ($\mu g\ L^{-1}$)						
13–17 m	25	2.18	4.97	0.225	6.16	1.64
20–25 m	16	0.186	0.165	0.087	0.382	0.083
33–38 m	25	0.102	0.096	0.012	0.181	0.046
$DMSP_p$ (nmol L^{-1})						
10–17 m	26	13.1	8.59	0.510	32.0	11.6
20–25 m	17	1.27	0.436	0.048	12.8	3.02
33–38 m	29	0.456	0.298	0.151	1.47	0.353
$DMSO_p$ (nmol L^{-1})						
10–17 m	18	1.25	1.29	0.342	2.24	0.568
20–25 m	9	0.322	0.283	0	0.986	0.290
33–38 m	19	0.136	0	0	2.08	0.466
$DMSP_d$ (nmol L^{-1})						
10–17 m	14	1.84	0.394	0.189	8.94	2.78
20–25 m	9	3.14	0.367	0.158	20.4	6.68
33–38 m	13	2.68	2.04	1.22	6.34	1.68
DMS (nmol L^{-1})						
10–17 m	23	1.23	0.550	0.041	6.21	1.88
20–25 m	16	42.2	61.9	0.067	96.3	36.7
33–38 m	27	254	268	167	337	48.8
$DMSO_d$ (nmol L^{-1})						
10–17 m	23	12.5	10.6	4.56	31.5	7.09
20–25 m	13	42.3	43.9	10.9	77.3	17.7
33–38 m	22	124	145	30.3	183	52.9

surface waters of both lobes are relatively low-salinity environments (<10), whereas the bottom waters are highly saline (>120). Furthermore, the water columns of each lobe are relatively cold (−5°C to 6°C). It should be noted that the water columns of these lakes have been hydraulically stable for perhaps the past 1,200 yr (Lyons et al. 2000), and many of these gradients may also have existed for the same time period (e.g., Priscu 1997). Consequently, the lack of vertical mixing means that the same water masses can be sampled from year to year.

Vertical profiles of Chl *a* are given in Fig. 1d for the west lobe and in Fig. 2d for the east lobe. The Chl *a* profiles, as with the profiles for the dimethylated-sulfur compounds, are the average of all measurements made during the 2000 field season. The range of Chl *a* concentrations, along with other statistical parameters for selected depth intervals, are given in Tables 1 and 2 for the west and east lobes of Lake Bonney, respectively. The concentrations and distributions of Chl *a* observed during this study are comparable to those of previous studies of Lake Bonney (Lizotte et al. 1996; Lizotte and Priscu 1998). Acrylate levels in the lake were consistently below the limit of detection (<3 nmol L^{-1}) in both lobes. These values contrasted significantly with those reported by Gibson et al. (1996), who observed acrylate concentrations ranging from below the limit of detection (<10 nmol L^{-1}) to over 1.2 μmol L^{-1} in coastal waters near Davis Station, East Antarctica.

Dimethylated-sulfur distribution—Summaries of the concentrations of the dimethylated-sulfur compounds found in the west and east lobes are tabulated in Tables 1 and 2, respectively. The results are summarized into three depth ranges that correspond, approximately, to the region of the Chl *a* maximum (10–15 m for the west lobe, 10–18 m for the east lobe), the chemocline (17–20 m for the west lobe, 20–25 m for the east lobe), and the lower salty layer (33–38 m for the west lobe, 33–37 m for the east lobe). Vertical profiles for $DMSP_p$ and $DMSO_p$ for the west lobe are given in Fig. 1d, and those for $DMSP_d$, DMS, and $DMSO_d$ are given in Fig. 1e. Maximum concentrations of $DMSP_p$ (up to 32 nmol L^{-1}) and $DMSO_p$ (up to 2.24 nmol L^{-1}) occurred in the upper layer at a depth of 13 m in the west lobe and coincided with the Chl *a* maximum (up to 6.16 μg L^{-1}). Maximum concentrations of $DMSP_d$ (up to 20.4 nmol L^{-1}), $DMSO_d$ (up to 183 nmol L^{-1}), and DMS (up to 337 nmol L^{-1}) all occurred at or near the bottom of the west lobe.

For the east lobe, the profiles for $DMSP_p$ and $DMSO_p$ are presented in Fig. 2d, and those for $DMSP_d$, DMS, and $DMSO_d$ are presented in Fig. 2e. Maximum concentrations of $DMSO_p$ (up to 1.89 nmol L^{-1}) and $DMSP_p$ (up to 5.21 nmol L^{-1}) occurred in the upper layer of the east lobe at depths of 13 and 18 m, respectively, which were deeper than the Chl *a* maximum (~3 μg L^{-1}) at 5 m. Maximum concentrations of $DMSP_d$ (up to 2.83 nmol L^{-1}) occurred at a depth of 13 m, whereas the highest levels of DMS (up to

Table 2. Mean, median, range, and standard deviation (SD) for Chl *a*, particulate DMSP ($DMSP_p$) particulate DMSO, dissolved DMSP, DMS, and dissolved DMSO for selected depth intervals in the east lobe of Lake Bonney. The summarized data are from samples collected during the austral summers of 1999–2000 and 2000–2001.

Variable	*n*	Mean	Medium	Minimum	Maximum	SD
Chl *a* ($\mu g\ L^{-1}$)						
10–18 m	18	0.726	0.736	0.100	1.34	0.334
20–25 m	17	0.247	0.252	0.055	0.489	0.134
33–37 m	8	0.282	0.220	0.143	0.498	0.122
$DMSP_p$ (nmol L^{-1})						
10–18 m	22	1.79	1.50	0.212	5.21	1.17
20–25 m	19	0.516	0.238	0.038	2.30	0.601
33–37 m	12	0.113	0.077	0	0.328	0.117
$DMSO_p$ (nmol L^{-1})						
10–18 m	16	0.991	1.06	0.275	1.89	0.468
20–25 m	14	0.348	0.408	0	0.715	0.256
33–37 m	7	0.238	0	0	1.21	0.502
$DMSP_d$ (nmol L^{-1})						
10–18 m	14	1.21	1.02	0.069	2.83	0.957
20–25 m	12	0.294	0.143	0	0.945	0.302
33–37 m	6	0.169	0.151	0	0.530	0.168
DMS (nmol L^{-1})						
10–18 m	21	1.37	0.087	0	3.78	1.14
20–25 m	18	23.5	18.1	2.20	68.6	21.3
33–37 m	11	6.14	6.61	1.30	8.26	2.07
$DMSO_d$ (nmol L^{-1})						
10–18 m	15	24.5	18.4	5.18	69.4	17.0
20–25 m	11	138	128	13.2	270	78.5
33–37 m	8	197	203	135	254	37.3

68.6 nmol L^{-1}) and $DMSO_d$ (up to 270 nmol L^{-1}) occurred in the lower layer at 22 m and 25 m, respectively. Profiles for ratios of $DMSP_p$:Chl *a,* $DMSO_p$:Chl *a,* and $DMSP_p$:$DMSO_p$ are presented in Figs. 1f and 2f for the west and east lobe, respectively. In the west lobe, the highest $DMSP_p$:Chl *a* ratios were found at a depth of 20 m in a region of high salinity below the Chl *a* maximum. The highest $DMSO_p$:Chl *a* ratios were observed near the bottom of the lake at a depth of 37 m, but this may have resulted from the arrival of degraded biomass from the surface layer. In the east lobe, the highest $DMSP_p$:Chl *a* and $DMSO_p$:Chl *a* ratios occurred at a depth of 20 m near the interface between in surface layer and the higher salinity bottom waters. Unlike the measurable concentrations of the dimethylated-sulfur compounds described in the preceding two paragraphs, $DMSO_2$ and methanethiol levels were consistently below the limits of detection for each compound throughout the course of the study.

Phytoplankton communities—Three taxonomic groups (chlorophytes, chrysophytes, and cryptophytes) accounted for more than 98% of the phytoplankton cells present in the east lobe of Lake Bonney and more than 99% of the cells present in the west lobe for the year 2000 sampling (Table 3). With respect to the individual species observed, *Chroomonas* sp. accounted for 92.6% of the cryptophytes in the east lobe and 92.3% in the west lobe. *Cryptomonas* sp. was the second most-abundant cryptophyte, accounting for 7.0% and 7.6% of the cryptophytes cells in the east and west lobes, respectively. The most abundant chrysophyte was *Ochromonas* sp., representing 99.1% and 99.2% of the chrysophyte cells present in the east and west lobes, respectively, with *Achnanthes* sp. contributing an additional 0.8% and 0.7%, respectively. *Chlamydomonas subcaudata* was the dominant chlorophyte, accounting for 92.5% and 87.5% of the chlorophyte community in the east and west lobes, respectively. *Chlamydomonas intermedia* contributed an additional 4.2% and 12.4% to the total chlorophyte cell count in the east and west lobes, respectively. *Chloromonas* sp. contributed a further 3.2% to the chlorophyte cell count in the east lobe.

Chloroform-inhibition experiments—Results from the inhibitor experiments conducted with water from 35 m and sediment material are presented in Fig. 3. No significant ($P > 0.05$) production of DMS was observed in the time-dependent slopes in experiments run for 16 h or 5 d. These results infer that no significant hydrolysis of DMSP to DMS is occurring within the lake.

Discussion

Dimethylated-sulfur concentrations—The most striking feature of the biogenic sulfur profiles is the high concentrations of DMS and $DMSO_d$ in the bottom layer of the west and east lobes, respectively. The DMS levels present near the bottom of the west lobe (up to 337 nmol L^{-1}, Table 1)

Table 3. Summary of the percent contribution of the three most dominant taxonomic groups to the phytoplankton community at selected depths in Lake Bonney, as determined by microscopy. The results are tabulated as the average (and range) percent contribution to the total number of cells present and the average (and range) of the percent contribution to the total phytoplankton carbon biomass. The summarized data are from samples collected during the austral summer of 2000–2001.

Location	Depth (m)	Chlorophytes		Chrysophytes		Cryptophytes	
		% cells	% biomass	% cells	% biomass	% cells	% biomass
West Bonney	5	2.0 (0.5–3)	12.0 (3–17)	89.9 (87–92)	63.0 (61–65)	8.0 (6–10)	24.7 (21–31)
	10	2.0 (0.9–3)	13.7 (11–17)	94.3 (89–97)	74.3 (58–84)	3.4 (1–8)	12.3 (3–31)
	13	15.1 (6–23)	42.7 (16–61)	80.2 (73–89)	43.3 (28–57)	3.1 (2–5)	14.0 (4–27)
	20	13.1 (4–25)	43.3 (31–59)	82.9 (73–90)	45.3 (37–54)	3.9 (2–7)	11.7 (4–25)
East Bonney	6	1.7 (0.3–2.9)	17.7 (0–27)	85.8 (83–89)	56.3 (50–69)	11.4 (8–13)	28.7 (23–39)
	10	6.3 (2–14)	32.0 (3–26)	90.5 (86–94)	69.7 (59–86)	2.7 (0.3–5)	9.0 (1–15)
	13	21.1 (12–35)	44.7 (30–67)	76.6 (63–86)	52.0 (31–68)	2.0 (1–3)	3.0 (1–6)
	18	45.1 (42–51)	75.7 (73–79)	47.5 (41–52)	15.7 (14–18)	6.8 (5–8)	8.3 (6–12)
	30	38.2 (35–43)	82.3 (72–90)	54.7 (51–60)	11.3 (7–15)	5.7 (3–10)	5.7 (2–12)

are amongst the highest observed in any freshwater environment or coastal salt pond. With the exception of hypersaline lakes in Canada, which have DMS concentrations of up to 3,050 nmol L^{-1} (Richards et al. 1994), concentrations in most lakes are generally below 200 nmol L^{-1} (e.g., Wakeham et al. 1987; Roberts et al. 1993; Simó et al. 1993; de Mora et al. 1996; Ginzburg et al. 1998). In oceanic environments, DMS levels are generally less than 10 nmol L^{-1} (Kettle et al. 1999), except during intense blooms of phytoplankton such as *Phaeocystis* sp., *Emiliania huxleyi*, or ice-algal communities, when DMS concentrations can exceed 300 nmol L^{-1} (Malin et al. 1992; DiTullio and Smith 1995).

The maximum $DMSO_d$ levels measured in the bottom waters of both the east (up to 270 nmol L^{-1}, Table 2) and west lobes (up to 183 nmol L^{-1}, Table 1) are among the highest reported for any aquatic environment. Richards et al. (1994) measured $DMSO_d$ concentrations up to 180 nmol L^{-1} in lakes and ponds on the Canadian Shield, and de Mora et al. (1996) found concentrations of up to 185 nmol L^{-1} in melt-water ponds near Bratina Island in McMurdo Sound. Conversely, $DMSO_d$ concentrations in the low-salinity surface waters in both lobes are typical of levels measured elsewhere in oceanic environments (Lee et al. 1999; Bouillon et al. 2002). In contrast to the elevated concentrations of DMS and $DMSO_d$, concentrations of $DMSP_d$ are relatively low throughout the water columns of both lobes of the lake. The maximum $DMSP_d$ concentrations found in Lake Bonney are comparable to concentrations observed in coastal salt ponds (up to 20 nmol L^{-1}; Wakeham et al. 1987), melt-water ponds (up to 8.4 nmol L^{-1}; de Mora et al. 1996), and at the lower end of the range observed in oceanic environments (up to 198 nmol L^{-1}; Turner et al. 1988). Total DMSP concentrations (dissolved + particulate) were considerably less than the maximum values (up to 1,400 nmol L^{-1}) reported by Richards et al. (1994).

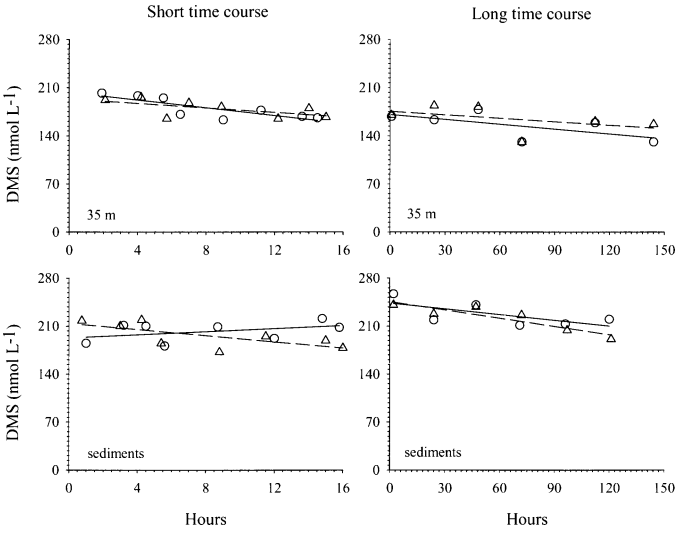

Fig. 3. Chloroform inhibitor experiments for samples from the west lobe. In each case, the solid line represents the best-fit straight line for the control samples (circles), and the dashed line represents the best-fit straight line for the treatment samples (triangles).

Interestingly, $DMSP_p$ concentrations in the upper water column of Lake Bonney were comparable to and, in some instances, such as the maximum values recorded in the west lobe, greater than those concentrations found in a wide variety of oceanic environments (up to 17 nmol L^{-1}; Turner et al. 1995; Matrai and Vernet 1997). Moreover, $DMSP_p$: Chl *a* ratios were relatively high (up to 29.1 nmol μg^{-1} in the east lobe and 103 nmol μg^{-1} in the west lobe). These values are similar to oceanic levels reported elsewhere (Turner et al. 1995; Matrai and Vernet 1997; Bouillon et al. 2002). They are also comparable to or greater than $DMSP_p$: Chl *a* ratios observed in ice-algal communities (Lee et al. 2001).

No $DMSO_p$ data currently exist for freshwater ecosystems. In contrast to $DMSP_p$, the concentrations of $DMSO_p$ observed in Lake Bonney are less than those measured in diatom-dominated ice-algal communities (Lee et al. 2001) and mixed oceanic communities (Simó et al. 1998), but they are similar to the lowest values reported for diatom-dominated seawater (Bouillon et al. 2002). However, $DMSO_p$: Chl *a* ratios reveal a slightly different pattern. The $DMSO_p$: Chl *a* ratios for the Lake Bonney phytoplankton community are similar to those for the communities studied by Simó et al. (1998) and Lee et al. (2001) and similar to the lowest values observed by Bouillon et al. (2002). This relationship indicates that the phytoplankton cells in Lake Bonney have a similar DMSO content to phytoplankton in oceanic environ-

ments and that the low levels of $DMSO_p$ may be due to relatively low amounts of Chl *a* found in the lake. Further discussion regarding the relationship between $DMSO_p$ and the phytoplankton community is presented in the following paragraphs.

Relationship between taxonomy and dimethylated-sulfur—Previous taxonomic studies on Lake Bonney have revealed that the phytoplankton are distributed in three distinct maxima, with each maxima dominated by different taxonomic groups (Lizotte et al. 1996; Lizotte and Priscu 1998). The results of our present study, both HPLC pigments and microscopy counts, were entirely consistent with these previous findings. From the ice-water interface to a depth of 8 m, chlorophytes (*Chlamydomonas* sp.) and cryptophytes (*Chroomonas lacustris*) dominated the algal community, with cryptophyte-specific pigments (i.e., alloxanthin) dominating the HPLC pigment results. From 8 m to 16 m, chrysophytes (*Ochromonas* sp.) were most abundant in terms of both cell counts and HPLC results (as indicated by fucoxanthin concentrations). Between 16 m and 20 m, chlorophytes (primarily *Chlamydomonas subcaudata*) and chrysophytes (*Ochromonas* sp.), were present with chlorophytes dominating the pigment signature (as indicated by chlorophyll *b* concentrations). The HPLC pigment signature also showed that alloxanthin was absent at 20 m in the east lobe. The results from HPLC-based pigment signatures were confirmed by direct microscopic observation.

The cryptophyte-dominated region of the water column near the ice–water interface contained relatively little $DMSP_p$ and the lowest $DMSP_p$: Chl *a* ratios. $DMSP_p$ concentrations were highest between 13 and 15 m in the west lobe and between 13 and 18 m in the east lobe, which coincided with the region of the water column dominated by chrysophytes, with increasing contributions from the chlorophyte community. $DMSO_p$: Chl *a* ratios were greatest at 20 m in both lobes, with much higher ratios being observed in the east lobe than in the west lobe. In the east lobe, chrysophytes dominated the phytoplankton community in terms of biomass, whereas chrysophytes and chlorophytes contributed equally to the biomass in the west lobe (Table 3). This region of the water column also corresponds to the chemocline, implying that the phytoplankton community is producing DMSP primarily as an osmoregulator (Vairavamurthy et al. 1985) rather than as an antioxidant (Sunda et al. 2002). In terms of DMSP-producing ability, chrysophytes can be relatively important producers, whereas cryptophytes and chlorophytes are typically poor producers (Keller et al. 1989). Three possibilities exist to explain the data from Lake Bonney. First, chrysophytes (particularly *Ochromonas* sp.) are the source of DMSP, but this does not explain satisfactorily the high $DMSP_p$: Chl *a* ratios in chlorophyte-dominated waters. Second, chlorophytes (particularly *Chlamydomonas subcaudata*), which do not normally produce DMSP, are producing DMSP in response to the increasing salinity. Third, DMSP production is due to a combination of the first two scenarios. Microscopy has also shown that the cryptophyte *Cryptomonas* sp. and the chlorophyte *Chlorella vulgaris* are present in Lake Bonney (Lizotte et al. 1996; Lizotte and Priscu 1998). Two known exceptions to the contention that cryptophytes and chlorophytes are poor producers of DMSP are a species of *Cryptomonas* and a species of *Chlorella* (Keller et al. 1989). Thus, although *Chlamydomonas subcaudata* and/or *Ochromonas* sp. appear to be the primary source of the DMSP, contributions from DMSP-producing strains of *Cryptomonas* and, to a lesser extent, *Chlorella* cannot be ruled out completely.

The findings of this study represent the first instance in which $DMSO_p$ has been shown to be present in significant levels in a freshwater ecosystem and in an algal assemblage dominated by cryptophytes, chlorophytes, and chrysophytes. The ecological role played by intracellular DMSO has yet to be determined, and the data from Lake Bonney reveal few clues. It has been hypothesized that DMSO may act as a free-radical scavenger (Lee and de Mora 1999; Lee et al. 2001). In the stratified phytoplankton community found in Lake Bonney (Lizotte et al. 1996; Lizotte and Priscu 1998), one might expect $DMSO_p$ concentrations or $DMSO_p$: Chl *a* ratios to be highest near the surface and to decrease with depth if the antioxidant hypothesis is correct, but this is not the case. However, such an observation is likely to be masked by species-dependent production of intracellular DMSO and adjustments in chlorophyll levels in response to light intensity (Prézelin 1981; Lee et al. 2001).

Biogeochemical cycle of dimethylated sulfur in Lake Bonney—A conceptual model for the dimethylated-sulfur cycle in Lake Bonney is presented in Fig. 4. This model is based on the results given in preceding paragraphs and the arguments developed in the following paragraphs. Previous studies have shown that Lake Bonney is divided by salinity-driven stratification into an upper trophogenic zone and a lower zone that is devoid of photoautotrophic activity (Lizotte et al. 1996; Spigel and Priscu 1998). Consequently, the sources and sinks of dimethylated sulfur in each layer are likely to be different. The profiles for DMS, $DMSP_d$, and $DMSO_d$ all show at least bimodal distribution of the compounds. Thus, the two layers of each lobe are considered to be two separate entities with respect to the cycling of dimethylated sulfur.

The sulfur cycle in the upper, low-salinity layer in each lobe is generally similar to the dimethylated-sulfur cycle found in the open ocean, with certain caveats caused by the perennial ice-cover. A very small amount of atmospheric exchange may occur through a moat that develops at the edge of the lake each summer, as is the case for nitrous oxide (Priscu 1997), but no exchange can occur through the permanent ice-cover that covers more than 97% of the lake's surface. The moat lasts for only about 10 weeks per year, and the lake ice is often grounded at the moat, making exchange through this conduit very low. Furthermore, DMS concentrations in the surface waters of the lake are not greater than those found in association with blooms of *Phaeocystis* sp. in the nearby Ross Sea during summer (DiTullio and Smith 1995), indicating that Lake Bonney is not an important regional source of DMS. Similarly, the ice-cover will severely reduce the quantity of dimethylated-sulfur compounds undergoing photochemical transformations, with only a few percent of the incident solar radiation penetrating the ice to the water column below (Howard-Williams et al.

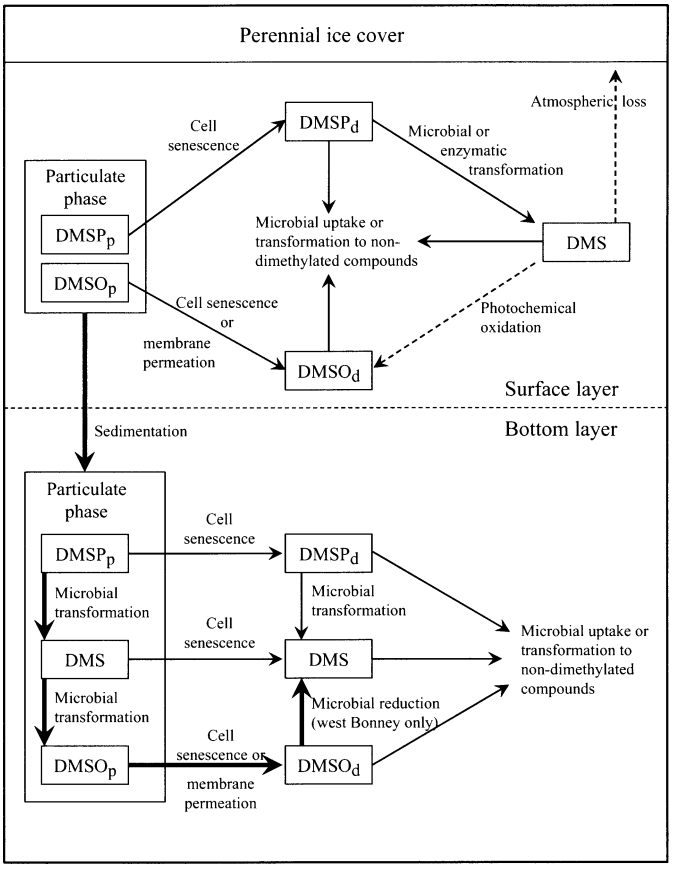

Fig. 4. Conceptual model for the biogeochemical cycling of dimethylated sulfur in Lake Bonney. The thin solid arrows indicate the dominant processes present in the lake. The thick solid arrows represent those processes that lead to the elevated levels of DMS and $DMSO_d$ found in the bottom waters of the lake. The dashed arrows represent those processes whose importance will be diminished because of the environmental conditions found in the lake.

1998). With these loss mechanisms either suppressed or absent from the surface waters of Lake Bonney, cycling of dimethylated sulfur will be predominantly via microbial transformations.

The other important pathway for the loss of dimethylated sulfur from the surface waters is most likely sedimentation of particulate material, which, in turn, will also be a source of dimethylated sulfur into the aphotic bottom waters of Lake Bonney. Continual input of sedimenting particles may partially explain the relatively high levels of DMS and $DMSO_d$ observed in the bottom waters of the lake. Hatton (2002) recently suggested that DMSP may be transformed to DMSO in sedimenting particles and hypothesized that DMSP was broken down enzymatically to DMS, which was subsequently oxidized by anaerobic or microaerophilic bacteria to DMSO. Hatton (2002) concluded that the transformation of DMSP to DMSO in sedimenting particulate matter could explain the origin of the relatively elevated levels of $DMSO_d$ in the deep ocean.

The same could hold true in the bottom waters of Lake Bonney. Preliminary analysis of samples using 16S rDNA sequencing has revealed the presence of a bacterium at 25 m in the west lobe that is 96% similar to *Methylophaga marina*, and in the case of a sample from 13 m in the east lobe, bacteria that are 96% similar to *Methylophaga marina* and 95% similar to *Methylophaga sulfidovorans* (Zehr and Priscu unpubl. data). The bacterium *Methylophaga sulfidovorans* is a known, aerobic DMS oxidizer (de Zwart et al. 1996). Furthermore, transformation of DMS to DMSO via ammonium and methane monooxygenases has also been observed in cultures of marine strains of nitrifiers (Juliette et al. 1993). Both the presence of nitrifiers and measurable rates of nitrification have been reported for Lake Bonney (Priscu 1997; Voytek et al. 1998). Our findings also show that carbon : nitrogen ratios change with depth in both lobes, indicating that sedimenting particulate material is undergoing biogeochemical processing. Moreover, our data reveal that $DMSP_p : DMSO_p$ ratios decrease with depth, which is consistent with DMSP being transformed to DMSO. Lisle and Priscu (in press) recently observed the presence of aggregates in the water column of Lake Bonney that are the equivalent of marine snow, and they found that these aggregates were ''hot-spots'' for microbial and viral activity, as is the case with marine snow (Azam and Long 2001). It is worth noting that dissolved organic carbon (DOC) concentrations increase dramatically in the bottom waters of each lobe, reaching levels in excess of 20 mg L^{-1} (Takacs and Priscu 1995, 1998). Such an increase could result from the conversion of particulate organic carbon to DOC, as is proposed for DMS and $DMSO_d$. However, heterotrophic activity in the waters below the chemocline is very low to nonexistent (Takacs and Priscu 1995, 1998; Ward et al. 2003), indicating that these conversions must be occurring very slowly.

Wakeham et al. (1987) found that anaerobic phototrophic bacteria were implicated in the cycling of DMS in a seasonally stratified coastal salt pond. This possibility is unlikely to occur, since the bottom waters of Lake Bonney are not anoxic and are aphotic. Some DMS may have resulted from the enzymatic cleavage of $DMSP_d$, but this cannot account for all of the DMS present. The enzymatic cleavage of DMSP results in the formation of equimolar amounts of acrylate and DMS, but measurements for acrylate reveal that acrylate concentrations are below about 3 nM at all depths in both lobes of Lake Bonney. Another potential DMS source is the disproportionation of two DMSO molecules into equimolar quantities of DMS and $DMSO_2$ (Lee and de Mora 1999). If the formation of $DMSO_2$ was taken as an indicator of the presence of this pathway, then up to 18 nmol L^{-1} of $DMSO_2$ could be produced before the pathway becomes detectable, and consequently up to 18 nmol L^{-1} of DMS. By this argument, all of the DMS present in the east lobe could have resulted from the disproportionation of DMSO. However, in the west lobe, only a small portion of the DMS present could have resulted from this pathway.

The methylation of methanethiol (Kiene and Capone 1988) can be ruled out as a source of DMS in Lake Bonney, since this pathway occurs in highly anoxic environments, and the waters and sediments of the west lobe are only suboxic. Moreover, no methanethiol was detected in the sediments or water column during our study. The lack of methanethiol also indicates that the degradation of DMSP into

non-DMS volatile sulfur compounds is not an important biogeochemical pathway in Lake Bonney, as has been found to be the case for seawater (Kiene and Linn 2000). This finding further implies that the assimilation of DMSP, and possibly of other dimethylated-sulfur compounds, is a key source of reduced sulfur for incorporation into bacterial biomass.

Another potential source for the dimethylated-sulfur compounds could be mats of cyanobacteria that may have existed in the lake in historical times. Extensive cyanobacterial mats are a feature of many lakes and ponds of the McMurdo Region. Priscu (1997) has suggested that some chemical gradients present in Lake Bonney might have resulted from the processes that formed the current lakes. The lake may have gone through an ice-free period that caused a drastic reduction in the volume of the lake through historic dry-down processes (Lyons et al. 2000). The east lobe in particular may have become isolated from input from the Taylor Glacier and been reduced to a hypersaline pond. Some evidence is available that cyanobacteria mats are unlikely to have been the sole source or, at the very least, the primary source of dimethylated sulfur in the deep waters of the lake. In the most saline melt-water ponds on the nearby McMurdo Ice Shelf, de Mora et al. (1996) found similar concentrations of $DMSP_d$, DMS, and $DMSO_d$. In hypersaline lakes of the Canadian Shield, Richards et al. (1994) observed very high levels of $DMSP_d$ and DMS levels, which were also considerably higher than those of $DMSO_d$. Thus, if the waters of the east lobe of Lake Bonney had dried down to a hypersaline or brine pond and mats of cyanobacteria were present, then one would expect relatively high concentrations of $DMSP_d$ and/or DMS. It is reasonable to assume that some dilution of water occurred as the lake refilled, but this would still result in DMS and $DMSP_d$ levels being relatively higher than $DMSO_d$ levels rather than the opposite relationship, which is observed in the east lobe of Lake Bonney.

Although sedimenting particulate matter may be the origin of the dimethylated-sulfur compounds in the bottom waters of the lake, the ultimate fate and subsequent distribution of these compounds is determined by redox chemistry. The bottom waters of the lake are suboxic, with the west lobe being slightly more reducing than the east lobe (between 325 mV and 400 mV and between 550 mV and 650 mV, respectively; Lee et al. 2004). Lee et al. (2004) estimated that the in situ reduction potential for the reduction of DMSO was slightly higher in the west lobe than the east lobe, leading them to hypothesize that this combination of factors made DMSO reduction more favorable as an energy source for bacteria in the west lobe than the east lobe. They concluded that DMSO reduction was thermodynamically unfavorable throughout the entire water column of the east lobe, allowing $DMSO_d$ levels to accumulate to the observed values. Conversely, DMSO reduction becomes thermodynamically favorable below 22 m in the west lobe (Lee et al. 2004), which is the approximate depth at which DMS begins to accumulate. However, two factors cannot be overlooked. First, although DMSO reduction may be unfavorable in the east lobe, some $DMSO_d$ (along with DMS and $DMSP_d$) will likely be lost as a result of bacterial uptake as a sulfur or carbon source. Second, although DMSO reduction is feasible in the west lobe, a large amount of $DMSO_d$ is still present. In both instances, uptake or reduction processes will be very slow because of low bacterial numbers and activity at the bottom of each lobe (Takacs and Priscu 1995, 1998; Ward et al. 2003).

Lake Bonney offers a unique system for the study of dimethylated-sulfur compounds. The low vertical mixing rates (mixing time for the water column is approximately 50,000 yr) allows gradients to persist for many years (up to the mixing time) and for gradients to be produced and maintained by very low rates of microbial activity. Although we could not detect transformations in these compounds, they may be occurring at rates well below the limits of detection associated with our experimental design. Scholten et al. (2003) have argued that using free-energy calculations may be a valuable tool for understanding the microbial cycling of DMSP, DMS, methanethiol, and related compounds in anoxic environments. Such thermodynamic approaches, including those discussed above for DMSO and DMS, along with stable isotope analyses may be the only way to identify the sources and sinks for the high levels of DMS and DMSO measured in Lake Bonney. Nonetheless, the coincident presence of these compounds with the high salinities and low temperatures found in Lake Bonney implies that they are produced as osmoregulators and cryoprotectants, allowing the organisms to survive in what would otherwise appear to be an inhospitable environment.

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