Antarctic Science 8 (1): 15–22 (1996)

Aspects of the biogeochemistry of sulphur in glacial melt water ponds on the McMurdo Ice Shelf, Antarctica

S.J. DE MORA[1*], P.A. LEE[1*], A. GROUT[1], C. SCHALL[2] and K.G. HEUMANN[2]

[1]*Chemistry Department, University of Auckland, Private Bag 92019, Auckland, New Zealand*
[2]*Institute of Inorganic Chemistry, University of Regensburg, 93040 Regensburg, Germany*
**Present address: Département d'océanographie, Université du Québec à Rimouski, 300 allée des Ursulines, Rimouski, Québec, Canada G5L 3A1*

Abstract: The distribution of dimethylsulphide (DMS), together with the precursor dimethylsulphoniopropionate (DMSP) and the oxidation product dimethylsulphoxide (DMSO), was measured in melt waters on the McMurdo Ice Shelf in the immediate vicinity of Bratina Island. Conductivity in these sulphate dominated ponds was extremely variable, ranging from 0.106–52.3 mS cm^{-1}. Similarly, chlorophyll *a* concentrations in the pond waters (1–150 $\mu g\ l^{-1}$) and mats (1.4–33 $\mu g\ cm^{-2}$) differed considerably. The biomass was dominated by benthic felts of phototrophic cyanobacteria, which might act as a source of biogenic sulphur compounds in the ponds. The mean (and ranges) of concentrations of dissolved sulphur compounds (nmol l^{-1}) were: CS_2 0.16 (<0.04–1.29); $DMSP_d$ 0.6 (<0.07–8.4); DMS 3.5 (<0.07–183); DMSO 27.9 (15.5–184.5). Very high concentrations of DMSO were ubiquitous in the ponds in the ice-cored moraine region of the ice shelf, with dissolved concentrations having been 1–2 orders of magnitude greater than those of DMS or $DMSP_d$. It is difficult to ascribe the formation of DMSO solely to the conventionally accepted pathways of DMS oxidation by either bacterial activity or photochemical reactions. A direct biosynthetic production from phytoplankton or bacteria might be involved which means that DMSO in aquatic environments could act as a significant source of DMS rather than as a sink as generally supposed.

Received 4 July 1995, accepted 14 December 1995

Key words: biogeochemical cycles, meltwater, ponds, DMS, DMSO, Antarctica

Introduction

Recent scientific curiosity in sulphur compounds has centred on dimethylsulphide (DMS) as this gas may play a significant role in the modification of global climate (Charlson *et al.* 1987). It has been postulated that DMS of marine biogenic origin evades to the atmosphere where it is oxidized thereby forming aerosols. The resulting aerosols, known as condensation nuclei (CN) and cloud condensation nuclei (CCN), affect the hydrological cycle and promote cloud formation. The major consequence of enhanced cloudiness in the marine troposphere is to increase the planetary albedo which in turn leads to a cooling effect. Thus, this mechanism may act as a biofeedback control to impede global warming caused by the increasing greenhouse gas concentrations in the atmosphere. A good correlation has been observed between atmospheric CN numbers and dissolved dimethylsulphoniopropionate ($DMSP_d$), the precursor of DMS, in the Antarctic Peninsula region (Kirst *et al.* 1993) and over the tropical South Atlantic Ocean (Andreae *et al.* 1994). DMSP, which behaves as an osmoregulator and cryoprotectant, is produced by phytoplankton (Kirst *et al.* 1991). Hence, $DMSP_d$ concentrations are often dependent upon the salinity of the water, but can be augmented by zooplankton grazing (Dacey & Wakeham 1986).

The biogeochemical cycling of DMSO in the aquatic environment remains poorly resolved (Malin *et al.* 1992). DMSO concentrations in oceanic waters may be an order of magnitude greater than those of DMS (Andreae 1980, Lee & de Mora, unpublished data). Bacteria can reduce DMSO to yield DMS (Zinder & Brock 1978). Alternatively, DMS in solution may be photochemically oxidized to DMSO (Brimblecombe & Shooter 1986) and so be prevented from venting to the atmosphere. Possible climatic control by the biogeochemical cycling of sulphur compounds is exerted through the air–sea exchange of DMS (Liss *et al.* 1993). To comprehend and model the availability of DMS requires knowledge of the partitioning of sulphur between DMS and DMSO.

It has been inferred from DMS photochemical oxidation studies (Brimblecombe & Shooter 1986) that DMSO in the marine environment is derived via such a pathway. Certainly the constant sunlight conditions encountered during the Antarctic summer would favour such a mechanism. Alternatively, DMSO production has been shown to occur as a result of DMS oxidation by phototrophic purple bacteria (Zeyer *et al.* 1987). Cyanobacteria comprise thick benthic mats in the McMurdo Ice Shelf aquatic ecosystem (Howard-Williams *et al.* 1989, Vincent *et al.* 1994) and such biota may similarly serve to convert DMS to DMSO.

This study examines the distribution of DMS, together with its precursor DMSP and the oxidation product DMSO, in melt waters on the McMurdo Ice Shelf in the immediate

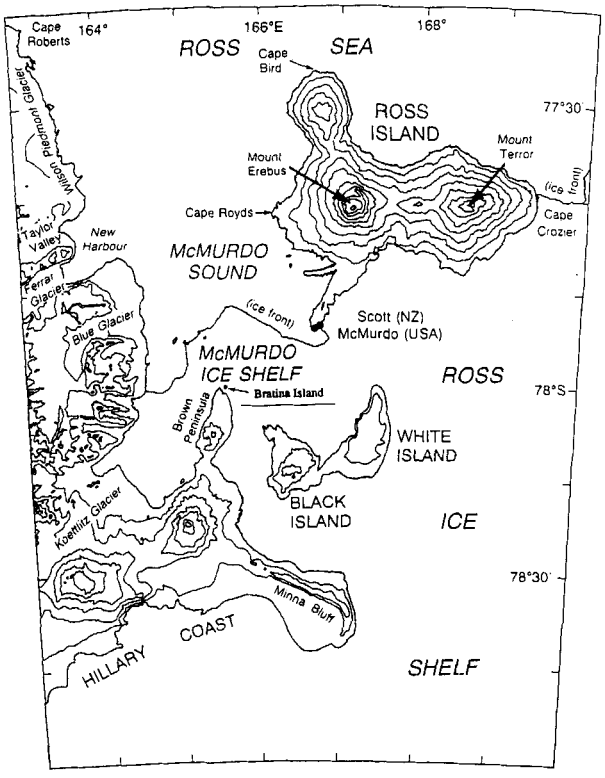

Fig. 1. Map of the McMurdo Ice Shelf showing Bratina Island.

vicinity of Bratina Island. Chlorophyll *a*, pH and major element concentrations were also measured. Microbial assemblages differ from one pond to another and the ponds in this region have proved to be valuable sites for examining microbial processes (Hawes *et al.* 1992, Howard-Williams *et al.* 1989, Vincent *et al.* 1993) and aqueous biogeochemistry (de Mora *et al.* 1994). In general, this particular ecosystem is relatively simple, being dominated by cyanobacteria and devoid of macroinvertebrate grazers. Moreover, the evolution of reduced sulphur gases in this environment has already been demonstrated (de Mora *et al.* 1990). Individual ponds can act as natural mesocosms, facilitating the study of geochemical and microbial processes that are expected to occur in widespread aquatic environments but which may be difficult to discern in more complex systems.

Environmental setting

Incorporating an area in excess of 1500 km^2, the melt water ponds and streams on the McMurdo Ice Shelf comprise the largest non-marine aqueous ecosystem within Antarctica (Fig. 1). There are two recognized terrain types in this region, namely "pinnacled ice" and "ice cored moraine" or "undulating ice". They are distinguished on the basis of geomorphological differences, but the chemical and biological characteristics of ponds in these two terrain types can differ markedly. The ponds are highly variable with respect to chemical composition, ranging from pristine glacial melt waters to hypersaline solutions of sodium sulphate (de Mora *et al.* 1994). Primary productivity similarly varies (Howard-Williams *et al.* 1989, Howard-Williams *et al.* 1990), but it is noteworthy that there are no macroinvertebrate grazers (Suren 1989). The biota is best characterized by the extensive, thick benthic mats of cyanobacteria which are dominated by oscillatoriacean species (Howard-Williams *et al.* 1990, Vincent *et al.* 1994). These pond systems serve as sources of biogenic gases for both sulphur containing (de Mora *et al.* 1990, Shooter *et al.* 1992) and halogenated (Schall *et al.* 1996) compounds.

Methods

Sampling

Overall, 130 samples from 30 different ponds from the ice cored moraine environment only of the McMurdo Ice Shelf were examined in January 1994. Emphasis was placed on a set of seven ponds which had been investigated during several previous seasons and for which a considerable body of information was available concerning their biological and chemical characteristics (de Mora *et al.* 1994, Hawes *et al.* 1993). These seven ponds were each sampled about 10 times during a two week period. Ponds are designated here by local unofficial names, but a map of the study area was produced in 1987 by the Department of Lands and Survey, New Zealand. 'Duet pond' and 'Fresh pond' are relatively large (1400 and 900 m^2 surface area, respectively) and remain covered with ice during the summer in most years. 'Skua pond' and 'Retro pond' are relatively small (275 and 140 m^2 surface area, respectively, and shallow (i.e. <1 m deep) ponds. Whereas 'Brack pond' has a surface area of 800 m^2, 'Salt pond' and 'Son of salt pond' are much smaller (130 and 5 m^2 surface area, respectively).

All surface water samples were taken from the edge of the pond using 1 l Nalgene LDPE bottles which had been pre rinsed with approximately 200 ml of sample water. Some subsurface samples (from only 10–30 cm) were collected using a Nalgene polysulphone filter flask and a Nalgene hand operated vacuum pump, being drawn up into the flask with a minimum amount of vacuum. The contents of the flask were then transferred to a 1 l Nalgene bottle. The sample bottles were filled to the brim to eliminate headspace and all liquid transfer processes were carried out in such a way as to avoid the premature degassing of the volatile sulphur compounds. At Bratina Island unfiltered aliquots (125 ml) of each sample were set aside for immediate DMS and $DMSP_d$ analyses, and conductivity and pH measurements. The rest of the sample was filtered through Whatman GF/F papers, with the papers being retained for chlorophyll *a* analyses. Aliquots (125 ml) of the filtrate were kept for subsequent DMSO determinations, and a further 250 ml aliquot was set aside for return to New Zealand for major ion analysis. All sample storage bottles had been washed in 2%

perchloric acid for 24 h, rinsed and soaked in Milli Q water (18 MΩ purity) for 48 h, and then air dried.

Conductivity, pH and chlorophyll a

Both water and benthic mat samples were analysed for chlorophyll *a*. Chlorophyll *a* was extracted by boiling in 95% ethanol for 5 min, followed by 24 h extraction at ambient temperature. The absorbance of the extract was then measured at 665 and 750 nm (Howard-Williams *et al.* 1989). The pH of the pond water samples was determined using an Orion Research SA250 Portable pH Meter with automatic temperature correcting probe. Regular on site calibration of the pH meter was carried out using NBS buffers. Conductivity was measured using a Suntex SC 12 Digital Conductivity Meter equipped with a Corning electrode using the appropriate cell constant and manual temperature correction. On return to New Zealand, the conductivities were remeasured under constant temperature conditions (15°C).

DMSO, DMSP and reduced sulphur gases

The analysis of all the organosulphur compounds was undertaken using a Perkin Elmer PE8500 gas chromatograph equipped with a sulphur specific flame photometric detector (GC FPD). Replicate DMSO analyses were carried out by direct injection of the filtered liquid sample into the GC using 1 μl or 5 μl Hamilton syringes. DMSO and $DMSO_2$ (dimethylsulphone) were isothermally separated at 150°C with retention times of *c.* 4.5 and 10 min respectively. The column train comprised a Teflon guard column (125 mm × 2.5 mm i.d.) and a Teflon analytical column (1.4 m × 2.5 mm i.d.), both packed with 15% Free Fatty Acid Phase (FFAP) on 40-60 mesh Chromosorb T. The flow rate of the carrier gas, oxygen free dry nitrogen, was 30 ml min^{-1}. The injector port temperature and the detector block temperature were set at 210°C. The injector glass liner was cleaned with Milli-Q water after every 50 injections to remove salt deposits. Sulphur hexafluoride (SF_6) was introduced into the H_2 flame to improve the sensitivity of the detector (de Mora *et al.* 1993, Farwell & Barinaga 1986). The detection limit for DMSO was 0.06 nmol l^{-1} and the detection limit for $DMSO_2$ was 0.16 nmol l^{-1}, with a RMS error for the analysis of 10%.

DMS and CS_2 were preconcentrated using a purge and trap technique based on the method described by de Mora *et al.* (1990). Oxygen free dry nitrogen (OFN, 80 ml min^{-1}) was bubbled through a 50 ml aliquot of filtered water sample for 10 min. The gas stream was passed through a scrubber tube containing K_2CO_3 to remove any water, followed by a sampling tube containing Molecular Sieve 5A where the sulphur compounds were trapped. The sampling train was held at ambient temperature during the sparging sequence. For subsequent analysis, the sampling tube was then connected to the gas sampling valve (in place of a sample loop) of the GC. The tube itself was placed into a block heater and ballistically heated to 320°C for two min. Thereafter, the gas valve was opened to allow the volatilized sample to be introduced onto the chromatographic column. The column used for the separation of the reduced sulphur gases was a 2 m × 2.5 mm i.d. Teflon column packed with Carbopack B/ 1.5% XE60/ 1% H_3PO_4 (Supelco Inc.). Temperature programming (2 min at 40°C, 25°C min^{-1}, 4 min at 140°C) was employed to achieve baseline separation of DMS and CS_2. Calibration of the volatile sulphur gases was carried out using permeation tubes (Shooter *et al.* 1992). The detection limits for DMS and CS_2 were 0.07 and 0.04 nmol l^{-1}, respectively.

The dissolved DMSP (denoted $DMSP_d$) was determined after conversion to DMS (White 1982). Following the sparging of DMS, 3 ml of 2 mol l^{-1} NaOH was added to the sample to hydrolyse $DMSP_d$ to DMS and the sample was then reanalysed for DMS as outlined above. To prevent any residual base from prematurely hydrolysing the next sample, the sparging unit was rinsed with 1 mol l^{-1} HCl followed by Milli Q water immediately after each $DMSP_d$ determination. The $DMSP_d$ detection limit was 0.07 nmol l^{-1} as DMS equivalents. The RMS Error for the analysis of both DMS and $DMSP_d$ was 12%.

Anion analyses

Simultaneous determination and quantification of the major anions was carried out using ion chromatography (Wylie 1993). A Dionex Model QIC instrument fitted with a conductivity detector was used for the analyses, with detector output to a Hewlett Packard 3396A Integrator. The eluent system used was bicarbonate/carbonate (2 mmol l^{-1} $NaHCO_3$/2 mmol l^{-1} Na_2CO_3) at a flow rate of 2 ml min^{-1}. The anion column train consisted of a Dionex HPIC AG4A guard column followed by a HPIC AS4A analytical column. On line suppression of the eluent conductivity was carried out using a Dionex AMMS suppressor, with suppressor column regeneration using 25 mmol l^{-1} H_2SO_4 at a flow rate of 5 ml min^{-1}. Samples were injected using a 50 μl sample loop.

Results

The conductivity in each of the principal seven ponds is shown in Fig. 2. The conductivities in these ponds encompass the limits to be encountered in waters on the McMurdo Ice Shelf, varying from *c.* 0.2 mS cm^{-1} in 'Fresh pond' and 'Duet pond' to 54.0 mS cm^{-1} in 'Son of salt pond'. The high salinity of 'Salt pond' and 'Son of salt pond' arises because these two pools are in contact with a small deposit of mirabilite. Hence, the ponds in this region span a wide range of sulphate concentrations. The pH in these ponds is quite high and typically falls in the range 8.5–10.5. The exception was 'Retro pond' which exhibited a median pH of 8.40, within a range of 7.77– 9.02. The high pH in these systems has been attributed to the photosynthetic activity of the benthic mats (de Mora *et al.* 1994, Hawes *et al.* 1993), but might include

https://doi.org/10.1017/S0954102096000041 Published online by Cambridge University Press

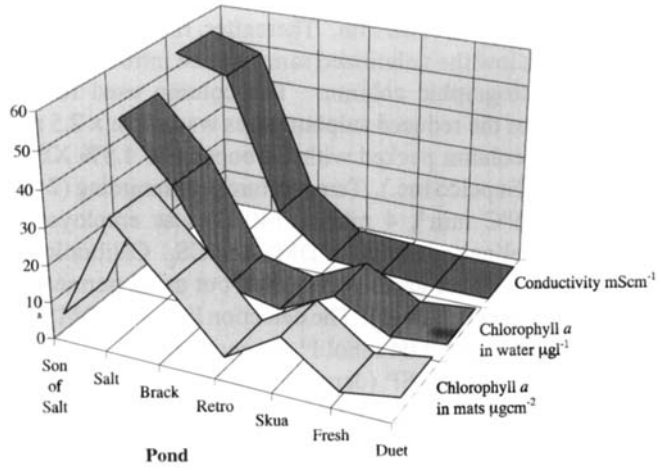

Fig. 2. Conductivity and mean chlorophyll *a* in plankton and benthic mats for the seven main study ponds near Bratina Island.

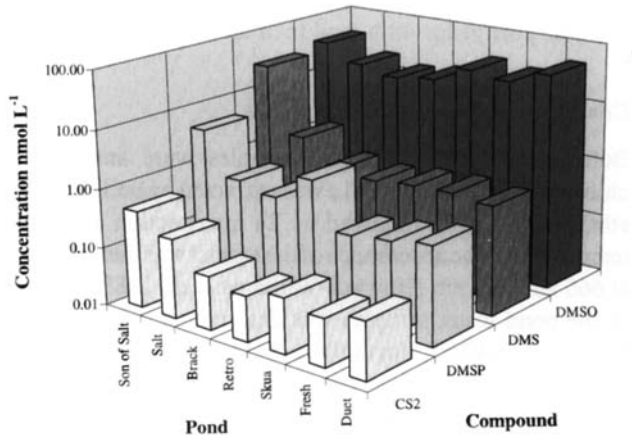

Fig. 3. Mean concentrations, plotted on an exponential scale, of CS_2, DMSP, DMS, and DMSO in the seven main study ponds near Bratina Island.

contributions from the dissolution of marine derived salts, especially calcite. The highest pH values in these ponds are likely to lead to the hydroxide-induced decomposition of DMSP to DMS (Dacey & Blough 1987).

For these seven ponds, the chlorophyll *a* content generally increased with the conductivity (Fig. 2). This trend is also evident for the chlorophyll *a* content of the benthic mats. The exceptional behaviour evident in 'Son of salt pond' has been noted previously (Vincent *et al.* 1994). As the water depth is only 1–2 m for these ponds, the biomass is dominated by the benthic cyanobacteria mats. However, it should be pointed out that carbon assimilation numbers are very low in comparison to those for the phytoplankton in overlying waters (Howard-Williams *et al.* 1989), i.e. 0.08 cf. 5–10 mg C (mg Chl *a*)$^{-1}$ h^{-1}. Accordingly, it is difficult to ascribe the biogenic source of sulphur compounds definitively to either the dominant biomass of the cyanobacterial mats or the rapid carbon assimilation rates of the phytoplankton. If data from all ponds are considered, there is no clear relationship between chlorophyll *a* and conductivity. Nevertheless, the highest chlorophyll *a* concentrations are in general associated with the most saline waters.

The distribution of sulphur compounds in the seven ponds is depicted in an exponential plot (Fig. 3). Although CS_2, $DMSP_d$, and DMS were found in all seven study ponds, each constituent was below the detection limit in some other ponds. In contrast, DMSO was detected in every pond investigated. $DMSP_d$ and DMS content apparently increased with the conductivity, ranging from 0.3–8.4 nmol l^{-1} and 0.7–30.1 nmol l^{-1}, respectively. Except in 'Son of Salt pond', the DMSO concentrations (15.5–48.7 nmol l^{-1}) were about an order of magnitude greater than those of DMS, and were not dependent upon the conductivity. For any given pond, the DMSO content from all surface samples was statistically indistinguishable from all subsurface (10–30 cm) samples. However, the ponds were highly variable from day to day and even within a given pond. For both 'Brack pond' and 'Salt pond', six replicate samples were collected from six sites in each pond at the same time. For any given set of analyses, the standard deviation varied from 4–9%. However, the DMSO concentrations varied in the range 90–338 and 206–1388 nmol l^{-1}, respectively, for the two ponds.

The relative composition of $DMSP_d$, DMS, and DMSO is shown in Fig. 4 for all ponds investigated. The overwhelming predominance of DMSO is evident. Exceptions occur with samples taken only from 'Salt pond' and 'Son of salt pond' which occasionally had elevated DMS concentrations. Low but notable concentrations of CS_2 were found, varying from 0.05–1.3 nmol l^{-1}, with high concentrations associated with the most saline/most biologically active ponds. $DMSO_2$ was not observed in any pond water samples, indicating that concentrations were consistently <0.16 nmol l^{-1}.

Discussion

DMSP is biosynthesized by phytoplankton, presumably for its properties as an osmoregulator and a cryoprotectant (Kirst *et al.* 1991). Accordingly, it has been suggested that aqueous $DMSP_d$ concentrations should be dependent upon the salinity. The $DMSP_d$ concentration as a function of conductivity for all ponds examined is shown in Fig. 5a. The absence of macroinvertebrates (Suren 1989) would limit the amount of DMS produced from DMSP released via cell rupture during grazing. Although the highest $DMSP_d$ concentrations were generally found in waters with the greatest conductivity, the relationship was not well established. The $DMSP_d$ was not related to planktonic chlorophyll *a* (Fig. 5b). This observation is well known since phytoplankton exhibit a marked inter-species variation in their ability to biosynthesize DMSP (Charlson *et al.* 1987, Keller 1989). However, the relationship could be further exacerbated in these ponds due to the dominance of benthic biota. Although all ponds are dominated

https://doi.org/10.1017/S0954102096000041 Published online by Cambridge University Press

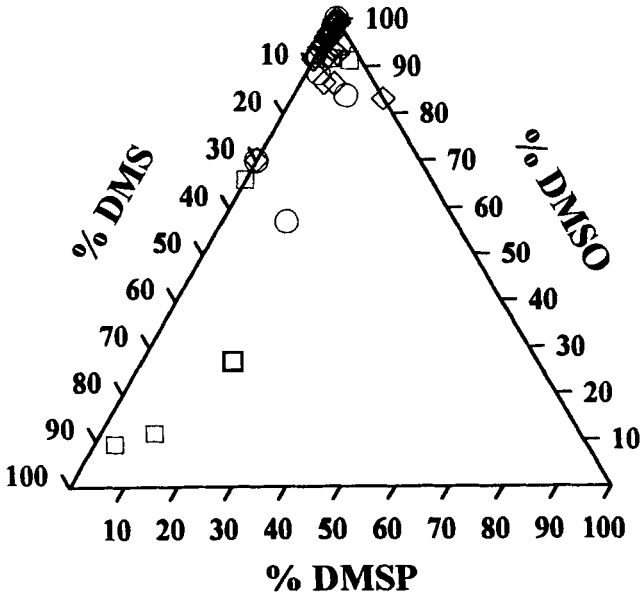

Fig. 4. Speciation of DMS-related organosulphur compounds in ponds atop the McMurdo Ice Shelf, whereby symbols represent samples from: □ Son of Salt pond, ◯ Salt pond and Δ 28 other ponds .

by cyanobacterial felts, there are inter-pond differences in taxonomic composition (Howard-Williams *et al.* 1989, Howard-Williams *et al.* 1990, Vincent *et al.* 1994).

$DMSP_d$ levels were found to vary from below the limit of detection to 8.4 nmol l^{-1}, with an average concentration of 0.6 nmol l^{-1} (standard deviation 1.6 nmol l^{-1}). The content of DMSP is evidently highly variable in natural waters. The $DMSP_d$ concentrations observed in the McMurdo Ice Shelf ponds are similar to the lowest values (4–20 nmol l^{-1}) determined in some Canadian lakes and wetland ponds (Richards *et al.* 1994). In contrast, this same study observed some much higher values (up to 1400 nmol l^{-1}) in hypersaline waters. Similarly, relatively elevated concentrations up to 20 nmol l^{-1} $DMSP_d$ were recorded in another so-named 'Salt pond', a seasonally stratified eutrophic basin on Cape Cod, Massachusetts, USA (Wakeham *et al.* 1987). A wide range in $DMSP_d$ concentrations has also been noted in oceanic environments. Data presented here are similar to values between 4 and 6 nmol l^{-1} reported for the surface waters in the Pacific Ocean (Hatton *et al.* 1994). However, higher concentrations have been observed elsewhere: 5.6–198 nmol l^{-1} in the North Sea and coastal waters near the British Isles (Turner *et al.* 1988) and 2–75 nmol l^{-1} in the Southern Ocean (Kirst *et al.* 1993). Thus, $DMSP_d$ in the melt water ponds falls within the lower range of concentrations typically encountered perhaps reflecting the limited bioproduction of $DMSP_d$ by cyanobacteria relative to phytoplankton (Keller *et al.* 1989). Alternatively, bacterial degradation of DMSP might be accelerated in this unusual ecosystem.

DMS is believed to be derived primarily from the enzymatic cleavage of DMSP, and hence, a relationship between $DMSP_d$

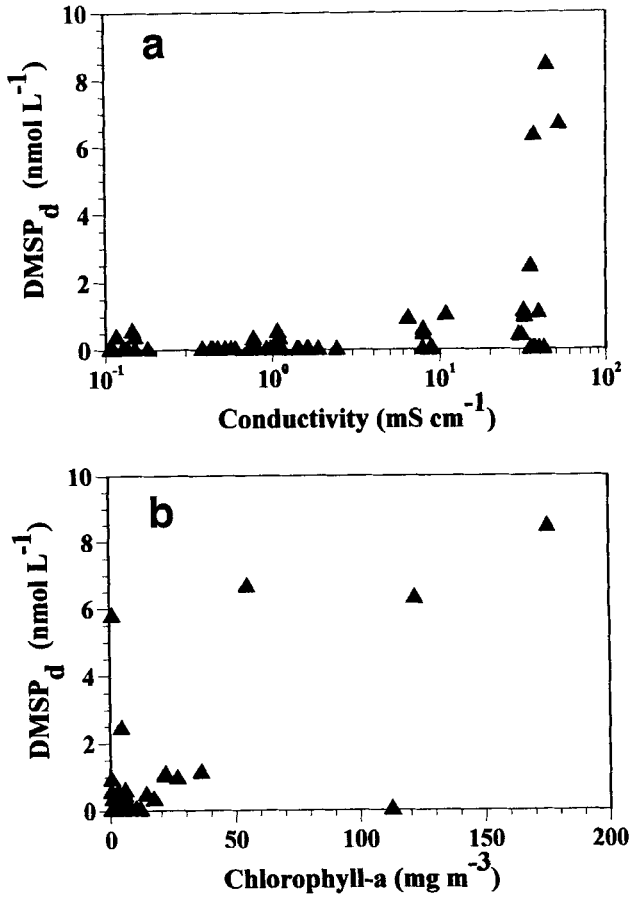

Fig. 5. **a.** $DMSP_d$ versus conductivity for all samples from 30 ponds on the McMurdo Ice Shelf. **b.** $DMSP_d$ versus chlorophyll *a* for samples from 30 ponds on the McMurdo Ice Shelf.

and DMS in solution would be expected. In these ponds, the highest aqueous DMS concentrations were indeed observed in those waters exhibiting the greatest $DMSP_d$ content. However, there was no consistent trend for DMS concentration with respect to the $DMSP_d$ content. A wide range of DMS levels was apparent for ponds exhibiting undetectable $DMSP_d$. The average DMS concentration for all the ponds analysed was 3.5 nmol l^{-1} (standard deviation 18.9 nmol l^{-1}, with a range of 0.2–183 nmol l^{-1}). For most ponds, the concentrations were comparable to the DMS levels encountered in 'Salt pond', Cape Cod, typically 5–10 nmol l^{-1} (Wakeham *et al.* 1987), and in oceanic environments, namely 1–30 nmol l^{-1} (Andreae & Barnard 1984, Turner *et al.* 1988). However, in the case of the more saline ponds, the large concentrations were vastly greater than oceanic values but remained less than the highest concentrations (3050 nmol l^{-1}) observed in Canadian hypersaline lakes (Richards *et al.* 1994).

Based on the observation that the DMS concentration was apparently enhanced in lakes with sulphate concentrations >20 mg l^{-1}, Richards *et al.* (1994) suggested that there was an unidentified mechanism present which increased the availability of sulphate leading to enhanced DMS production. Similarly, a tendency of increased dissolved DMS in sulphate

https://doi.org/10.1017/S0954102096000041 Published online by Cambridge University Press

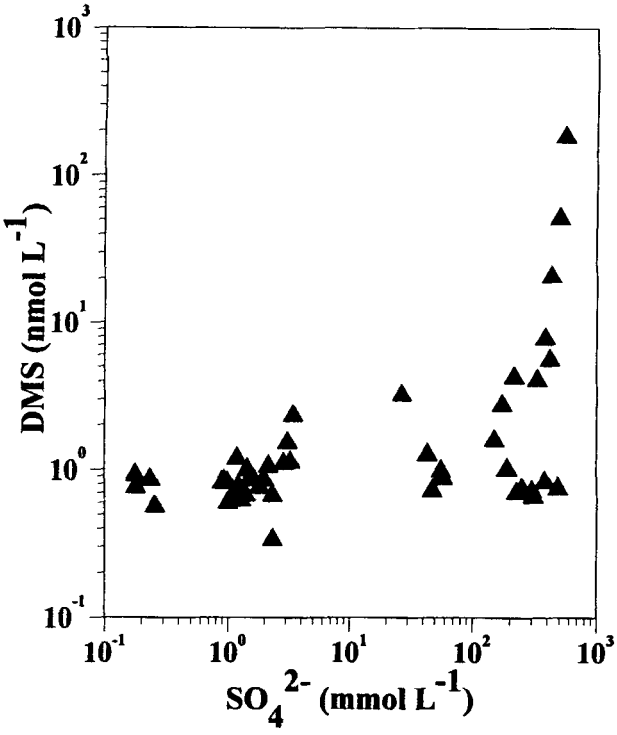

Fig. 6. DMS versus sulphate for all samples from 30 ponds on the McMurdo Ice Shelf.

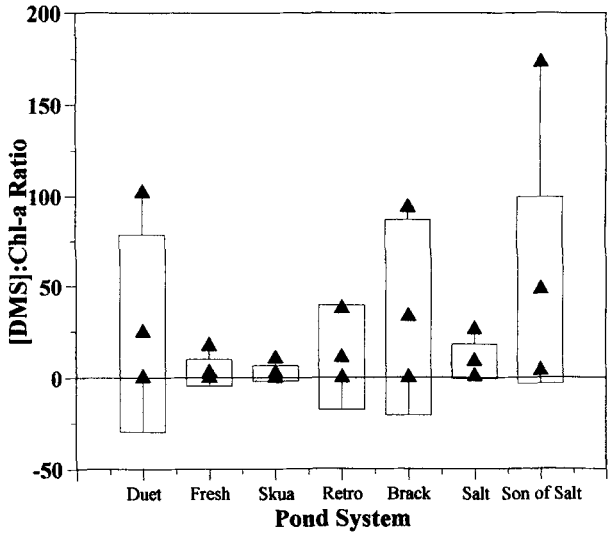

Fig. 7. Mean [DMS]: mean chlorophyll *a* ratio for the seven main study ponds near Bratina Island. In this box and whisker diagram, the triangles indicate the mean and range of the ratio and the box itself illustrates the 95% confidence interval for the ratio.

enriched waters was found on the McMurdo Ice Shelf (Fig. 6). However, this trend also followed the rise in the chlorophyll *a* levels with increasing conductivity of the pond waters. Thus, it is difficult here to attribute the behaviour to the presence of an "availability" mechanism or simply to the increasing biological activity. Ratios for [DMS]: chlorophyll *a* were found to vary considerably, mainly due to the large variations in DMS concentrations presumably as a result of wind induced degassing of the ponds. Although the seven main study ponds showed some disparity in the average value of the [DMS]: chlorophyll *a* ratio for each pond, the values were not significantly different (Fig. 7). No general correlation was observed between DMS and chlorophyll *a*. As with the DMSP correlations, the chlorophyll *a* measurements do not take into account any variations in the taxonomic composition of the phytoplankton and their ability to produce DMS. In general, the ratios for the overlying waters were found to be 2–4 orders of magnitude less than oceanic values (Iverson *et al.* 1989) but 1–2 orders of magnitude greater than values observed in some Canadian hypersaline systems (Richards *et al.* 1994). This observation coupled with the high concentration of DMS detected, in some cases much higher than oceanic values, would strongly suggest that the cyanobacterial mats were the primary source of the biogenic sulphur gases.

The DMSO concentrations found in the hypersaline ponds on the McMurdo Ice Shelf were quite elevated, with the highest value being 185 nmol l^{-1}. This is comparable to the maximum value of 180 nmol l^{-1} found in Canadian lakes and wetland ponds (Richards *et al.* 1994). Lower concentrations, <22 nmol l^{-1} were observed in 'Salt pond', Cape Cod (Wakeham *et al.* 1987). In contrast, the DMSO content in surface oceanic waters is typically <15 nmol l^{-1} (Bates *et al.* 1994, Kiene & Gerard 1994), and decreases with depth (Andreae 1980, Ridgeway *et al.* 1991, Hatton *et al.* 1994). Although concentrations up to 218 nmol l^{-1} have been observed, such values may have been anomalously high because analytical techniques employing reduction methods are subject to interference from the reduction of DMSP and other readily reducible sulphur compounds (de Mora *et al.* 1993, Hatton *et al.* 1994). More recently, DMSO specific techniques have given levels in the range 3–14 nmol l^{-1} in the equatorial Pacific Ocean (Hatton *et al.* 1994) and up to 106 nmol l^{-1} in coastal waters of New Zealand (Lee & de Mora, unpublished data). This later study clearly demonstrates seasonal and diurnal variations in DMSO content.

As noted previously, DMS can be oxidized to DMSO either by photochemical reactions (Brimblecombe & Shooter 1986) or by phototrophic purple bacteria (Zeyer *et al.* 1987). Regardless of the production mechanism, the subsequent build up of ambient DMSO concentrations would require low degradation (or assimilation) rates, but this is generally a feature of Antarctic microbial systems (Vincent 1988). If DMS was converted to DMSO by either of these processes, then one might expect a relationship to exist between DMS and DMSO; but this was not observed. The DMSO levels were independent of aqueous DMS concentrations (Fig. 8), and also with respect to conductivity and the dissolved sulphate content. An alternative possibility exists to account for the high ambient concentrations of DMSO, namely via a

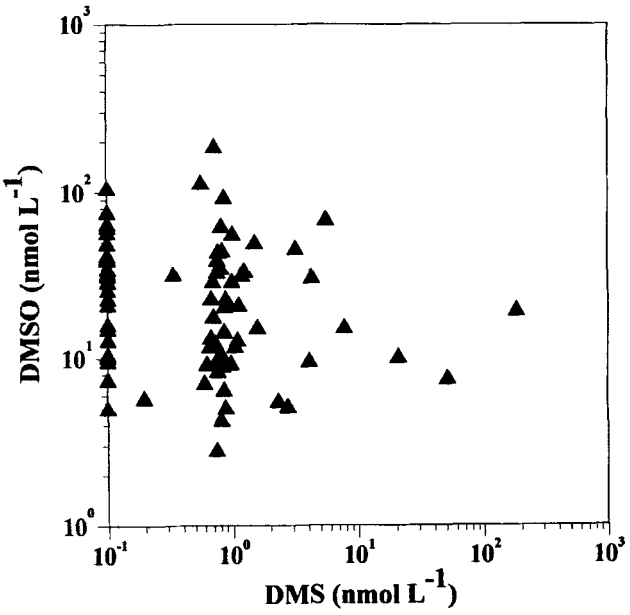

Fig. 8. DMSO versus DMS for all samples from 30 ponds on the McMurdo Ice Shelf.

direct biosynthetic pathway. It is widely recognized that DMSO is naturally present in various foodstuffs and beverages (de Mora *et al.* 1993, Pearson *et al.* 1981). Furthermore, DMSO has been observed to be present in monocultures of several marine phytoplankton indicating that DMSO production is not strictly a result of DMS oxidation by photochemical processes or bacterial activity (Andreae 1980). During January 1994, 'Duet pond' and 'Fresh pond' had >90% ice coverage thereby preventing the evasion of biogenic DMS to the atmosphere and potentially limiting the photochemical oxidation of DMS to DMSO. Nonetheless, DMS levels remained relatively low and even these ponds had relatively copious amounts of DMSO. On the basis of the high DMSO levels shown here in fresh waters having little DMS, we speculate that the biosynthesis of DMSO does indeed represent an important source to the biogenic DMSO pool, and hence, cannot be ignored. Confirmation of the extent and importance of direct DMSO production via a biochemical pathway requires incubation experiments and the investigation of particulate DMSO in natural waters. It should be noted that the unusual assemblage of brominated and iodinated organic compounds found in these systems has also been linked to the photosynthetic activity of the cyanobacteria mats (Schall *et al.*1996).

The behaviour of CS_2 was interesting, having been present in most ponds sampled, including all seven main study ponds (Fig. 3). This volatile reduced sulphur compound had previously been measured in marine waters just west of Bratina Island (Shooter *et al.* 1992) and had been found in the atmosphere at Bratina Island (de Mora *et al.* 1990), indicating that the ponds were a significant source of CS_2. Similarly, CS_2 has been detected in water samples taken from hypersaline Canadian (Richards *et al.* 1994) and Spanish lakes (Simó *et al.* 1993). In contrast, in Organic Lake, a hypersaline lake (>130‰) in the Vestfold Hills, CS_2 , could be detected only in the sediments (Roberts *et al.* 1993). A sedimentary source for CS_2 has also been postulated in 'Salt pond', Cape Cod (Wakeham *et al.* 1987). The origin of CS_2 in glacial melt water ponds of the McMurdo Ice Shelf remains unknown, but probably involves leakage from the beneath the cyanobacterial mats where anoxic conditions occur.

Conclusions

Very high concentrations of DMSO were ubiquitous in the McMurdo Ice Shelf ponds in Antarctica, with dissolved concentrations having been 1–2 orders of magnitude greater than those of DMS or $DMSP_d$. It is difficult to ascribe the formation of DMSO solely to the conventionally accepted pathways of DMS oxidation by photochemical reactions and bacterial activity. A direct biosynthetic production from phytoplankton or bacteria might be involved with the important implication that DMSO in aquatic environments could act as a significant source of DMS rather than a sink as generally supposed.

Acknowledgements

In Auckland, we greatly appreciate the efforts of Bill Pepper, Dave Newton, and Ron Bryant in constructing various pieces of equipment. In Antarctica, we are grateful to the staff of Scott Base, and the pilots and crew of US Navy Squadron VXE 6 and No.3 Squadron, RNZAF, for logistic support. We acknowledge with gratitude the encouragement shown by staff of the New Zealand Antarctic Programme throughout the RISE study and especially appreciate their support for this international collaboration. We thank our colleagues in the RISE programme, notably Warwick Vincent and Clive Howard-Williams, for their enthusiasm and many useful discussions. We also thank Warwick Vincent and two anonymous referees for comments on an earlier version of this manuscript. This investigation was financed by the University of Auckland Research Committee and the Deutsches Forschungsgemeinschaft.

References

ANDREAE, M.O. 1980. Dimethylsulfoxide in marine and freshwaters. *Limnology and Oceanography*, **25**, 1054–1063.

ANDREAE, M.O., ELBERT, W. & DE MORA, S.J. 1994. Biogenic sulfur emissions and aerosols over the tropical South Atlantic. 3. Atmospheric dimethylsulfide, aerosols and cloud condensation nuclei. *Journal of Geophysical Research*, **C100**, 11335–11356.

ANDREAE, M.O. & BARNARD, W.R. 1984. The marine chemistry of dimethylsulfide. *Marine Chemistry*, **14**, 267–279.

BATES, T.S., KIENE, R.P., WOLFE, G.V., MATRAI, P.A., CHAVEZ, F.P., BUCK, K.R., BLOMQUIST, B.W. & CUHEL, R.L. 1994. The cycling of sulfur in surface seawater of the northeast Pacific. *Journal of Geophysical Research*, **C99**, 7835–7843.

BRIMBLECOMBE, P. & SHOOTER, D. 1986. Photo-oxidation of dimethylsulfide in aqueous solution. *Marine Chemistry*, **19**, 343–353.

CHARLSON, R.J., LOVELOCK, J.E., ANDREAE, M.O. & WARREN, S.G. 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature*, 326–655.

DACEY, J.W.H. & BLOUGH, N.V. 1987. Hydroxide decomposition of dimethylsulfoniopropionate to form dimethylsulfide. *Geophysical Research Letters*, **14**, 1246–1249.

DACEY, J.W.H. & WAKEHAM, S.G. 1986. Oceanic dimethylsulfide: production during zooplankton grazing on phytoplankton. *Science*, **233**, 1314–1316.

DE MORA, S.J., GROUT, A. & SHOOTER, D. 1990. The analysis of reduced sulfur gases in air and melt waters by gas chromatography at Bratina Island, 78°S. *New Zealand Antarctic Record*, **10**, 12–21.

DE MORA, S.J., LEE, P., SHOOTER, D. & ESCHENBRUCH, R. 1993. The analysis and importance of dimethylsulfoxide in wine. *American Journal of Enology and Viticulture*, **44**, 327–332.

DE MORA, S.J., WHITEHEAD, R.F. & GREGORY, M. 1994. The chemical composition of glacial melt water ponds on the McMurdo Ice Shelf, Antarctica. *Antarctic Science*, **6**, 17–27.

FARWELL, S.O. & BARINAGA, C.J. 1986. Sulfur-selective detection with the FPD: Current enigmas, practical usage, and future directions. *Journal of Chromatographic Science*, **24**, 483–494.

HATTON, A.D., MALIN, G., MCEWAN, A.G. & LISS, P.S. 1994. Determination of dimethyl sulfoxide in aqueous solution by an enzyme-linked method. *Analytical Chemistry*, **66**, 4093–4096.

HAWES, I., HOWARD-WILLIAMS, C. & PRIDMORE, R.D. 1993. Environmental control of microbial biomass in the ponds of the McMurdo Ice Shelf, Antarctica. *Archives of Hydrobiology*, **127**, 271–287.

HAWES, I., HOWARD-WILLIAMS, C. & VINCENT, W.F. 1992. Desiccation and recovery of Antarctic cyanobacterial mats. *Polar Biology*, **12**, 587–594.

HOWARD-WILLIAMS, C., PRIDMORE, R., DOWNES, M.T. & VINCENT, W.F. 1989. Microbial biomass, photosynthesis and chlorophyll *a* related pigments in the ponds of the McMurdo Ice Shelf, Antarctica. *Antarctic Science*, **1**, 125–131.

HOWARD-WILLIAMS, C., PRIDMORE, R.D., BROADY, P.A. & VINCENT, W.F. 1990. Environmental and biological variablity in the McMurdo Ice Shelf ecosystem. *In* KERRY, K.R. & HEMPEL, G., *eds. Antarctic ecosystems: ecological change and conservation*. Berlin: Springer-Verlag, 23–31.

IVERSON, R.L., NEARHOOF, F.L. & ANDREAE, M.O. 1989. Production of dimethylsulfonium propionate and dimethylsulfide by phytoplankton in estuarine and coastal waters. *Limnology and Oceanography*, **34**, 53–67.

KELLER, M.D. 1989. Dimethyl sulfide production and marine phytoplankton: the importance of species composition and cell size. *Biological Oceanography*, **6**, 375–382.

KELLER, M.D., BELLOWS, W.K. & GUILLARD, R.R.L. 1989. Dimethylsulfide production in marine phytoplankton. *In* SALTZMAN, E.S. & COOPER, W.J., *eds. Biogenic sulfur in the environment*. Washington, DC: ACS, 167–182.

KIENE, R. & GERARD, G. 1994. Determination of trace levels of dimethylsulfoxide (DMSO) in seawater and rainwater. *Marine Chemistry*, **47**, 1–12.

KIRST, G.O., THIEL, C., NOTHNAGEL, J., WANZEK, M. & ULMKE, R. 1991. Dimethylsulphoniopropionate (DMSP) in ice-algae and its possible biological role. *Marine Chemistry*, **35**, 381–388.

KIRST, G.O., WANZEK, M., HAASE, R., RAPSOMANIKIS, S., DE MORA, S.J., SCHEBESKE, G. & ANDREAE, M.O. 1993. Ecophysiology of ice algae (Antarctica): Dimethylsulfoniopropionate content and release of dimethylsulfide during the icemelt. *In* RESTELLI, G. & ANGELETTI, G., *eds. Dimethylsulfide: oceans, atmosphere and climate*. Dordrecht: Kluwer, 23–36.

LISS, P., MALIN, G. & TURNER, S. 1993. Production of DMS by marine phytoplankton. *In* RESTELLI, G. & ANGELETTI, G., *eds. Dimethylsulfide: oceans, atmosphere and climate*. Dordrecht: Kluwer, 1–14.

MALIN, G., TURNER, S.M. & LISS, P.S. 1992. Sulfur: the plankton/climate connection. *Journal of Phycology*, **28**, 590–597.

PEARSON, T.W., DAWSON, H.J. & LACKEY, H.B. 1981. Natural occurring levels of dimethyl sulphoxide in selected fruits, vegetables, grains, and beverages. *Journal of Agriculture and Food Chem*istry, **29**, 1089–1091.

RICHARDS, S.R., RUDD, J.W.N. & KELLY, C.A. 1994. Organic volatile sulfur in lakes ranging in sulfate and dissolved salt concentration over five orders of magnitude. *Limnology and Oceanography*, **39**, 562–572.

RIDGEWAY, R.G.J., BANDY, A.R. & THORNTON, D.C. 1991. Determination of aqueous dimethyl sulfide using isotope dilution gas chromatography/mass spectrometry. *Marine Chemistry*, **33**, 321–34.

ROBERTS, N.J., BURTON, H.R. & PITSON, G.A. 1993. Volatile organic compounds from Organic Lake, an Antarctic, hypersaline, meromictic lake. *Antarctic Science*, **5**, 361–366.

SCHALL, C., HEUMANN, K.G., DE MORA, S. & LEE, P. 1996. Biogenic brominated and iodinated organic compounds in ponds on the McMurdo Ice Shelf, Antarctica. *Antarctic Science*, **8**, 45-49.

SHOOTER, D., DE MORA, S.J., GROUT, A., WYLIE, D.J. & ZHI-YUN, H. 1992. The chromatographic analysis of reduced sulfur gases in Antarctic waters following the pre-concentration onto Tenax. *International Journal of Environmental Analytical Chemistry*, **47**, 239–249.

SIMÓ, R., DE WIT, R., GRIMALT, J.O. & ALBAIGÉS, J. 1993. Dimethylsulphide and other volatile organic sulfur compounds in some neglected ecosystems: a study in evaporitic environments and in sulphate-rich karstic lakes. *In* RESTELLI, G. & ANGELETTI, G., *eds. Dimethylsulfide: oceans, atmosphere and climate*. Dordrecht: Kluwer , 173–181.

SUREN, A. 1989. Microfauna associated with algal mats in melt water ponds on the Ross Ice Shelf. *Polar Biology*, **10**, 329–335.

TURNER, S.M., MALIN, G., LISS, P.S., HARBOUR, D.S. & HOLLIGAN, P.M. 1988. The seasonal variation of dimethyl sulfide and dimethylsulfoniopropionate concentrations in nearshore waters. *Limnology and Oceanogr*aphy, **33**, 364–375.

VINCENT, W.F. 1988. *Microbial ecosystems of Antarctica*. Cambridge: Cambridge University Press, 304 pp.

VINCENT, W.F., CASTENHOLZ, R.W., DOWNES, M.T. & HOWARD-WILLIAMS, C. 1993. Antarctic cyanobacteria: light, nutrients and photosynthesis in the microbial mat environment. *Journal of Phycology*, **29**, 745–755.

VINCENT, W.F., DOWNES, M.T., CASTENHOLZ, R.W. & HOWARD-WILLIAMS, C. 1994. Community structure and pigment organisation of cyanobacteria-dominated microbial mats in Antarctica. *European Journal of Phycology*, **28**, 213–221.

WAKEHAM, S.G., HOWES, B.L., DACEY, J.W.H., SCHWARZENBACH, R.P. & ZEYER, J. 1987. Biogeochemistry of dimethylsulfide in a seasonally stratified pond. *Geochimica Cosmochimica Acta*, **51**, 1675–1684.

WHITE, R.H. 1982. Analysis of dimethylsulfonium compounds in marine algae. *Journal of Marine Research*, **40**, 529–536.

WYLIE, D.J. 1993. *Atmospheric chemistry of biogenic sulfur in the Southern Hemisphere*. PhD thesis. University of Auckland, 303 pp. [Unpublished.]

ZEYER, J., EICHER, P., WAKEHAM, S.G. & SCHWARZENBACH, R.P. 1987. Oxidation of dimethyl sulfide to dimethyl sulfoxide by phototrophic purple bacteria. *Applied and Environmental Microbiology*, **53**, 2026–2032.

ZINDER, S.H. & BROCK, T.D. 1978. Dimethyl sulphoxide reduction by micro-organisms. *Journal of General Microbiology*, **105**, 335–342.