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Volatile organic compounds from Organic Lake, an Antarctic, hypersaline, meromictic lake

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Abstract: Five volatile organic compounds were identified throughout 1991 in the hypolimnion of Organic Lake. These were dimethylsulphide (DMS), dimethyldisulphide (DM2S), dimethyltrisulphide (DM3S), dimethyltetrasulphide (DM4S) and phenol. The concentration of these compounds increased with lake depth. The concentration of DMS and DM2S was higher in the sediment than in the water column. Carbon disulphide occurred only in the sediment. DMS was the only volatile organic compound detected in the epilimnion of the lake, where its concentration increased from winter onwards. The source of DMS was not dimethylsulphoniopropionate (DMSP). This was determined by hydroxylation of the sample with NaOH. There was no change in the concentration of DMS but the concentration of DM2S increased dramatically while the concentrations of DM3S and DM4S decreased concomitantly. This has important implications in the estimation of DMS derived from DMSP by hydroxylation when organic polysulphides are also present. The stability of the hypolimnion of Organic Lake was reflected by the lack of change in temperature, density, redox potential and the relatively constant concentration of volatile organic compounds throughout the year. Potential sources of the volatile organic compounds are discussed in relation to the isolated nature of the lake.

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Introduction

The importance of dimethylsuphide (DMS) and other reduced sulphur compounds (RSC) from the oceans in climate control and the sulphur budget has received considerable attention (Lovelock *et al.* 1972, Andreae *et al.* 1983, Steudler & Peterson 1984, Charlson *et al.* 1987, Andreae 1990). Organic Lake is located in the Vestfold Hills, Antarctica (78°18'E, 68°26'S), and is ice covered about nine months of the year. It is a small, highly saline, meromictic lake, *c.* 7 m deep. The anoxic zone is devoid of O_2 and H_2S but contains very high levels (up to 300 n $g\,l^{-1}$) of DMS, the source of which has not been determined (Deprez *et al.* 1986, Franzmann *et al.* 1987, Gibson *et al.* 1991). To further the study of RSC and other volatile organics in Organic Lake we used a Gas Chromatograph-Mass Selective Detector (GC-MSD) during 1991.

Materials and methods

Sampling

Water samples were collected from Organic Lake throughout 1991 using a modified 2 l polycarbonate Kemmerer bottle deployed either through a hole drilled through the ice when present or from a small boat. Samples were collected in order of depth to avoid disturbing the water column. Water was transferred from the sampler into a new plastic bag to ensure thorough mixing of the sample. Subsamples were then poured quickly into a 500 ml Schott bottle (with teflon lined cap), a 28 ml McCartney bottle and a 250 ml plastic Duranol. These samples were for volatile organic analysis, redox measurements, and algal enumeration respectively. The first two bottles were filled to the brim before capping and all samples were transferred to the laboratory in an insulated container to avoid freezing. It is realized that the step involving the plastic bag could allow oxygen contamination of the sample as well as possible loss of volatiles. However, provided the transfer was carried out quickly and smoothly, there appeared to be little if any differences between sampling directly from the bottle compared with the plastic bag. In the laboratory, 0.5 ml of Lugol's solution was added to each Duranol. These were stored at 4°C until analysis. The Schott bottles were temporarily stored at 1°C, in the dark. Samples for E_h measurements were allowed to equilibrate to room temperature. Analysis of volatile organic compounds and E_h took place within 24 h of sampling.

Sediment samples were obtained using either a modified piston sampler in winter (King & Everitt 1980), or a box sampler in summer. Sediment was transferred to a glass jar, filled to the brim, stored, and analysed for volatile organic compounds within 24 h of sampling.

Physical parameters

Temperature and conductivity, recorded with a Submersible Data Logger (Platypus Engineering, Hobart, Tasmania), were used to calculate conductivity at 20°C and then density at 20°C (g salt l^{-1}) using the formulas described by Gibson *et al.* (1990). Redox potential was measured with an Activon platinum redox electrode.

Algae enumeration

Samples for algal counts were concentrated from 100 ml to 5 ml by standing for 48 h. They were then transferred to settling chambers and allowed to stand for a further 24 h. Cells were viewed by phase contrast microscopy; 10 fields of view were counted at 400x magnification.

Chemical analysis

Fifteen ml of each water sample was transferred to a 20 ml head space analysis vial containing 4 g of anhydrous Na_2SO_4. The Na_2SO_4 was added to enhance the "salting out effect", which decreased the solubility of the volatile organic compounds and increased their concentration in the head space. Sediment samples were transferred to 20 ml head space analysis vials without anhydrous Na_2SO_4, and the volume of sediment in the vial was made up to the same total volume as the water samples (with salt added). No salt was added to the sediment samples since it did not dissolve. To each sample vial 25μl of internal standard was added before being capped and vortexed. All samples were prepared in triplicate. The internal standard of 100μl cyclohexanone in 100 ml water, was intended to allow comparison of the concentration of volatile organics at different depths and over time by expressing concentration as a percentage of the internal standard peak area of the Total Ion Chromatogram.

Volatile organics were extracted using a Hewlett-Packard 19395A Head Space Analyser (HSA), and separated and identified (with an authentic spectral library) using a Hewlett-Packard 5890-II Gas Chromatograph and a 5971A Mass Selective Detector (GC-MSD). The HSA and GC-MSD operating conditions are shown in Table I. In 1991 Gibson *et al.* reported their detection limits of DMS using a purge and trap linked to a GC with a Flame Photometric Detector, as approximately 10 ng l^{-1}. By comparison our detection limit of DM2S and phenol (using the MSD in scan mode) was 1μg l^{-1} and 5000 μg l^{-1} respectively. dimethyldisulphide (DMS), dimethyltrisulphide (DM3S), dimethyltetrasulphide (DM4S) and carbon disulphide (CS_2) were not quantified. By extrapolation of the DM2S concentration it is possible to estimate their concentrations.

Table I. Head Space Analyser (HSA) and Gas Chromatograph-Mass Selective Detector (GC-MSD) operating conditions.

Head Space Analyser	
Carousel temperature	80°C
Sample loop temperature	85°C
Sample loop volume	1 ml
Transfer loop temperature	150°C
Gas Chromatograph	
Injector temperature	160°C
Split ratio	20:1
Column head pressure	25 psi
Column	SGE 50 m BP1
Internal diameter	0.22 mm
Film thickness	0.25μm non polar methyl silicone
Linear velocity	29 cm S^{-1}
Oven start temperature	5°C
Equilibration time	30 sec
Initial time	3 min
Initial rate	10°C min^{-1}
Halt temperature	150°C
Time	2.5 min
Final rate	20°C min^{-1}
Final temperature	250°C
Final time	2 min
Mass Selective Detector	
Solvent delay	4 min
Electron multiplier voltage	1450-1550 V
Mass scan range	29-250
Approximate scans S^{-1}	3
Ionization	70 eV
Threshold	1000

Results

Physical parameters of the lake in winter and summer are shown in Table II. Below 4 m, the redox potential, temperature and density were relatively stable compared with the surface layers throughout the year. The surface water temperature was coldest in October (-10.8°C, ice thickness 60 cm) and warmest in January (+14.4°C, ice free). The greatest difference in surface density occurred between these months (133 g salt l^{-1} in October and 45 g salt l^{-1} in January). The low density in January was due to the ice melting and a lack of mixing with the water below.

The two predominant algal species in the lake were identified from morphological characteristics as *Dunaliella* sp. and *Chaetoceros* sp. Similar numbers of each were found and they appeared to decrease in number from May (30–40 x 10^5 l^{-1}) to November (6–8 x 10^5 l^{-1}). Their distribution was fairly constant in the epilimnion.

The seasonal changes of DMS concentration throughout the lake are shown in Table III. Samples taken prior to September were collected with an unmodified Kemmerer bottle and are not presented here. The concentration of DMS generally increased with depth, and was greatest in the sediment. The concentration was relatively stable throughout the year at depths 6 and 7 m (*c.* 120μg l^{-1}) and in the sediment. Samples from the oxycline (5 m) varied in concentration throughout the year and may have resulted from small differences in sampling depth between sampling dates. The samples collected from 5 m contained both oxic and anoxic water and a slight inaccuracy in sample collection would greatly affect the concentrations detected. The

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Table II. Winter and summer profiles of the physical parameters measured in Organic Lake. The oxycline occurs between 4–5 m and is indicated by a reduction in redox potential and an increase in salinity (- = no measurement taken).

	4 September 1991 (55 cm ice)			23 December 1991 (ice free)		
depth (m)	temperature (°C)	redox (mV)	salinity (g salt l^{-1})	temperature (°C)	redox (mV)	salinity (g salt l^{-1})
surface	-10.3	-	130	-	-	-
1	-10.3	+311	131	+10.4	+252	140
2	-10.3	+290	131	-4.1	+246	145
3	-10.3	+283	132	-8.6	+241	145
4	-9.9	+271	132	-8.8	+232	147
5	-7.0	+139	171	-7.5	+98	182
6	-5.1	-93	173	-6.0	-72	182
7	-4.6	-137	-	-5.3	-127	-

concentration of DMS in the epilimnion generally increased from winter to summer.

Fig. 1 shows a typical profile of the volatile organic compounds identified at each depth in October. Compounds were identified from mass spectra and concentration is expressed as a percentage of the internal standard. This approach was necessary as it could not be foreseen which compounds would be detected prior to analysis. The most abundant compound was DMS, followed by DM2S, DM3S, phenol, DM4S and carbon disulphide. Their maximum concentrations in the water column at this date were approximately 110, 36, 40, 10000, 1.5, and 1μg l^{-1} (estimated from the DM2S and phenol standards). The concentration of most volatiles was higher in the sediment than in the water column at 7 m. Two exceptions were DM3S and DM4S; the latter was not detected at all in the sediment.

Table III. Seasonal changes of DMS concentration (as a % of internal standard) in Organic Lake during 1991. (- = no measurement taken).

	Sampling dates (1991)				
Depth (m)	4/9	8/10	1/11	2/12	23/12
1	3	-	-	5	0
2	3	11	17	11	47
3	2	13	19	23	46
4	2	11	27	32	47
5	78	77	148	38	141
6	533	448	496	-	358
7	563	482	531	535	745
sediment	491	589	633	557	-

Discussion

Gibson *et al.* (1991) proposed that in meromictic lakes of the Vestfold Hills containing high (>18.6 ng l^{-1}) DMS concentrations, either the degradation processes is relatively less efficient, or more DMS is produced in response to increased salinity. The high salinity of the lake has also reduced the species diversity in the epilimnion so that the only eucaryotes observed were two types of algae (*Dunaliella* sp. and *Chaetoceros* sp.), and a choanoflagellate *Acanthaoecopsis unguiculata* (van den Hoff & Franzmann 1986). Franzmann *et al.* (1987) noted that highest DMS concentrations occurred with the highest number of *Dunaliella* in the lake. However, they noted that pure cultures of *Dunaliella* sp. did not produce DMS in culture headspaces. They isolated strains of the bacterium *Halomonas* sp. that produced DM2S from methionine and cysteine. Only two of the 25 strains tested produced DMS and methyl mercaptan (MSH). They suggested that the main source of DMS was probably bacterial degradation of sulphur-containing compounds, some of which may have originated from algal cells. DM2S has been produced *in vitro* in comparable concentrations to the *in situ*

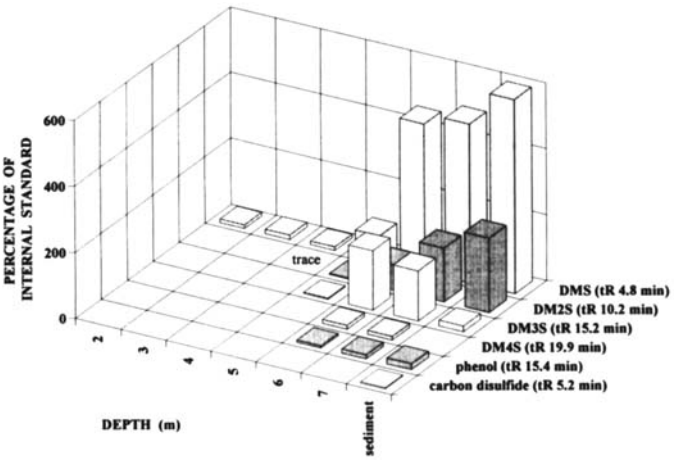

Fig. 1. Relative concentrations (as a % of internal standard) of the organic volatiles present in the water column and sediment Organic Lake in October 1991. (tR = retention time)

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DMS concentration (Holdsworth & Roberts unpublished data), at the same time, trace quantities of DMS and DM3S were also detected. This was achieved by inoculating a small amount of Organic Lake sediment into an artificial Organic Lake media containing methionine as the sole source of carbon. The cultures were grown initially anaerobically and in the light; DM2S was produced in cultures that grew bacteria only as well in cultures that grew both bacteria and algae.

Deprez *et al.* (1986) and Franzmann *et al.* (1987) reported that the depth of maximum DMS concentration in Organic Lake was at or just above the oxycline. This phenomena has also been observed in a seasonally stratified coastal salt pond in Salt Pond, Massachusetts (Wakeham *et al.* 1984, Wakeham *et al.* 1987). In Organic Lake, however, this result may be attributed to the use of an unmodified Kemmerer bottle for sampling which was shown to leak during retrieval (Roberts & Burton 1993). During 1991 the highest concentration of DMS occurred at the bottom of the lake which implies that DMS was produced anaerobically. Garrick & Gibson (1987) also reported highest levels of DMS below the oxycline but they also detected the highest concentrations of DMSP at the same depth. They measured DMSP by the method of White (1982), which relies on the assumption that DMS, released from samples upon the addition of NaOH, can be measured to determine the concentration of DMSP in original samples. When we repeated this method on Organic Lake samples, no change in the DMS concentration was observed. However, the peak area of DM2S increased by a factor of five whilst the concentrations of DM3S and DM4S decreased by a similar amount (Roberts 1991). Thus DMSP was not present in our samples. It is not known what Garrick & Gibson (1987) measured by the hydrolysis technique since their system was reported as being capable of resolving DM2S from DMS. The poor correlation between measured DMSP maximum and algal number would suggest they did not measure DMSP. Hence the main production of DMS and the organic polysulphides would appear to be anaerobic degradation of sulphur compounds but not simply from the breakdown of DMSP.

Kadota & Ishida (1972), Drotar *et al.* (1987), Kiene & Taylor (1988a & b), Kiene & Capone (1988), Kelly & Baker 1990, Kelly & Smith (1990) and Kiene *et al.* (1990) have proposed several pathways for anaerobic production of DMS, depending on the sulphur compounds being degraded. These pathways utilize 3-mercaptopropionate (3-MPA) or MSH as intermediates for the breakdown of sulphur containing amino acids and DMSP. The 3-MPA is transformed into a number of reduced sulphur components including DMS and DM2S. Methyl mercaptan may give rise to DMS after methylation by microorganisms, and DM2S by oxidation and dimerization. Henatsch & Juttner (1990) found that MSH was the major volatile sulphur compound in the anoxic layers of a stratified lake (Schleinsee, SW Germany) and the concentration increased from the metalimnion to the sediment. DMS was only found near the sediment. However, whilst MSH was probably not detectable on our system, Deprez *et al.* (1986) and Gibson *et al.* (1991) did not detect MSH with their systems which were capable of retaining and separating MSH and DMS. Anaerobic production of MSH and DMS is stimulated by the addition of methoxylated aromatic compounds (Finster *et al.* 1990) but the process requires H_2S which was not present in Organic Lake.

The gradual increase in DMS concentration from September–December in the upper 4 m of the lake was possibly the result of algal production or breakdown of algae in the epilimnion. It was associated with the increase in sunlight hours (six weeks without direct sunlight in winter). The temperature and density of the surface waters remained fairly constant. However, algal numbers did not correlate with DMS concentration which suggests that it was not simply due to an increase in algal numbers.

The presence of the organic polysulphides had not been previously reported in Organic Lake. Cool (4°C) manual injections of head space samples showed the presence of the polysulphides (Roberts 1991). The production of the polysulphides from the reaction of MSH and elemental sulphur at room temperature (McMillan & King 1948) and at the sample heating temperature of 80°C (Gschwend *et al.* 1982) would not appear to be occurring here since MSH is not present in the lake. Decomposition and disproportionation of the polysulphides (Kende *et al.* 1965, Chubachi *et al.* 1967, Pickering *et al.* 1967, Wajon *et al.* 1985, Kohnen *et al.* 1989) also does not appear to have occurred since the ratios of polysulphides to DMS were stable when heated at 80°C for *c.* 24 h (Roberts 1991). It is possible that DM2S may have arisen from the oxidation of DM3S under headspace analysis conditions (Tarbell 1961, Henatsch & Juttner 1990). The absence of MSH in Organic Lake (Deprez *et al.* 1986, Gibson *et al.* 1991) would appear to preclude it as a potential source of polysulphide production during head space analysis. On the other hand MSH can be produced from the oxidation of amino acids to DM2S and further oxidized to thiosulphinate ester which then proceeds through an unstable intermediate (sulphenic acid) reacting with H_2S to produce DM3S and water (Maruyama 1970, Miller *et al.* 1973). In Organic Lake the lack of MSH and H_2S could conceivably be due to the rapid production of polysulphides from these products rather than simply from the exclusion of the anaerobes that produce them. Gschwend *et al.* (1982) suggested that dimethyl polysulphides may be derived from sulphur containing metabolites other than MSH, for example cyclic polysulphides and acyclic forms. Wajon & Wilmot (1992) suggested that a naturally occurring chemical reaction between polysulphide (S_n^{2-}) with methyl iodide may also produce DM3S.

The increase in DMS and DM2S concentration in the sediment and decrease in DM3S and DM4S concentration could be due to a number of factors including different rates of production and degradation. Alternatively DM3S and DM4S may be produced from chemical reactions only occurring in water column or transformed to DM2S in the sediment, or chemically bound to the sediment.

In Organic Lake carbon disulphide was detected in the sediment only and in concentrations far lower than DMS. This agrees with the results of Gibson *et al.* (1991) who did not detect

it in the water column of Organic Lake and Deprez *et al.* (1986) who measured very small amounts using a purge and trap system. Similarly in Salt Pond (Massachusetts) the concentration of carbon disulphide was far lower than that of DMS and it was thought to originate from the sediment (Wakeham *et al.* 1987). Henatsch & Juttner (1990) detected low amounts of carbon disulphide in the hypolimnion only of Lake Schleinsee (SW Germany), and in salt marshes it was only a small fraction of the total gaseous sulphur released (Steudler & Peterson 1984). In the open ocean it was produced under anaerobic conditions in the sediment where it was thought to participate in the transfer of sulphur from the sediment back to the surface waters (Lovelock 1974, Zehnder & Zinder 1980). The sources of carbon disulphide appear to be the same as those mentioned above for the dimethyl sulphides (except DMSP), but, it does not appear to be anaerobically transformed like the methylated sulphides (Kelly & Smith 1990).

Phenol was the only non-sulphur containing volatile organic compound satisfactorily identified. Its abundance was relatively low but remained constant between 6 and 7m with little increase in the sediment. Phenol is produced by anaerobic catabolism of aromatic amino acids by clostridia (Elsden *et al.* 1976, Elsden & Hilton 1979) and by microbial degradation of benzene (Laskin & Lechevalier 1984), in sewage sludge-derived methanogenic enrichments (Grbic-Galic 1986) and in lichens (Vicente 1991). The lack of phenol in Organic Lake above 6m suggests that it may be produced near the sediment. Alternatively, since it is degraded by a wide range of microorganisms, it could be consumed as fast as it is produced in the shallower depths.

Conclusions

Reduced sulphur volatiles in Organic Lake are derived principally from the anaerobic breakdown of the algae by bacteria. The high concentration of DM2S and trace levels of DMS and DM3S produced *in vitro,* and the lack of DMSP *in situ* shows that the source of reduced sulphur compounds is not predominantly DMSP as is the case in Antarctic ocean waters. The standard method of quantifying DMSP by hydrolysis to DMS leads to serious errors in the presence of polysulphides and thus their absence must be established before the standard method of White (1982) can be used.

The importance of bacteria in the production of DMS from this hypersaline lake suggests that the role of bacteria in the production of DMS from the ocean should be examined more carefully.

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References

ANDREAE, M.O. 1990. Ocean-atmosphere interactions in the global biogeochemical sulphur cycle. *Marine Chemistry*, **30**, 1-29.

ANDREAE, M.O., BARNARD, W.R. & AMMONS, J.M. 1983. The biological production of dimethylsulphide in the ocean and its role in the global atmospheric sulphur budget. *In* HALLBERG, R. *ed.*, Environmental Biogeochemistry. *Ecological Bulletins (Stockholm),* **35**, 167-177.

CHARLSON, R.J., LOVELOCK, J.E., ANDREAE, M.O. & WARREN, S.G. 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature*, **326**, 655-661.

CHUBACHI, S., CHATTERJEE, P.K. & TOBOLSKY, A.V. 1967. Reaction of dimethyl tetrasulphide with unsaturated compounds. *Journal of Organic Chemistry*, **32**, 1511-1517.

DEPREZ, P.P., FRANZMANN, P.D. & BURTON, H.R. 1986. Determination of reduced sulphur gases in Antarctic lakes and seawater by gas chromatography after solid adsorbent preconcentration. *Journal of Chromatography*, **362**, 9-21.

DROTAR, A.M., BURTON, A.G., TAVERNIER, J.E. & FALL, R. 1987. Widespread occurrence of bacterial thiol methyltransferases and the biogenic emission of methylated sulphur gases. *Applied and Environmental Microbiology,* **53**, 1626-1631.

ELSDEN, S.R. & HILTON, M.G. 1979. Amino acid utilization in clostridial taxonomy. *Archives of Microbiology*, **123**, 137-141.

ELSDEN, S.R., HILTON, M.G. & WALKER, J.M. 1976 The end products of the metabolism of aromatic amino acids by clostridia. *Archives of Microbiology*, **107**, 283-288.

FRANZMANN, P.D., DEPREZ, P.P., BURTON, H.R. & VAN DEN HOFF, J. 1987. Limnology of Organic Lake, Antarctica, a meromictic lake that contains high concentrations of dimethyl sulphide. *Australian Journal of Marine and Freshwater Research*, **38**, 409-417.

FINSTER, K., KING, G.M. & BAK, F. 1990. Formation of methylmercaptan and dimethylsulphide from methoxylated aromatic compounds in anoxic marine and freshwater sediments. *FEMS Microbiology Ecology*, **74**, 295-302.

GARRICK, R.C. & GIBSON, J.A.E. 1987. *Annual Report to the Australian Antarctic Division.* Kingston: Australian Antarctic Division, 145 pp.

GIBSON, J.A.E., FERRIS, J.M., VAN DEN HOFF, J. & BURTON, H.R. 1990. Temperature-density, temperature-conductivity and conductivity-density relationships for marine-derived saline lake waters. *ANARE Research Notes,* No. 75. 1-31.

GIBSON, J.A.E., GARRICK, R.C., FRANZMANN, P.D., DEPREZ, P.P. & BURTON, H.R. 1991. Reduced sulphur gases in saline lakes of the Vestfold Hills, Antarctica. *Palaeogeography Palaeoclimatology Palaeoecology*, **84**, 131-140.

GRBIC-GALIC, D. 1986. Anaerobic production and transformation of aromatic hydrocarbons and substituted phenols by ferulic acid - degrading BESA - inhibited methanogenic consortia. *FEMS Microbiology Ecology*, **38**, 161–191.

GSCHWEND, P.M., ZAFIRIOU, O.C., MANTOURA, R.F.C., SCHWARZENBACH, R.P. & GAGOSIAN, R.B. 1982. Volatile organic compounds at a coastal site. I. Seasonal variations. *Environmental Science and Technology*, **16**, 31-38.

HENATSCH, J.J. & JUTTNER, F. 1990. Occurrence and distribution of methane thiol and other volatile organic sulphur compounds in a stratified lake with anoxic hypolimnion. *Archiv für Hydrobiologie*, **119**, 315-323.

KADOTA, H. & ISHIDA, Y. 1972. Production of volatile sulphur compounds by microorganisms. *Annual Review of Microbiology*, **26**, 127-138.

KELLY, D.P. & BAKER, S.C. 1990. The organosulphur cycle: aerobic and anaerobic processes leading to turnover of C1-sulphur compounds. *FEMS Microbiology Reviews*, **87**, 241-246.

KELLY, D.P. & SMITH, N.A. 1990. Organic sulphur compounds in the environment: Biogeochemistry, microbiology and ecological aspects. *Advances in Microbial Ecology*, **11**, 345-385.

KENDE, I., PICKERING, T.L. & TOBOLSKY, A.V. 1965. The dissociation energy of the tetrasulphide linkage. *Journal of the American Chemical Society*, **87**, 5582-5586.

KIENE, R.P. & CAPONE, D.G. 1988. Microbial transformations of methylated sulphur compounds in anoxic salt marsh sediments. *Microbial Ecology*, **15**, 275-291.

KIENE, R.P., MALLOY, K.D. & TAYLOR, B.F. 1990. Sulphur-containing amino acids as precursors of thiols in anoxic coastal sediments. *Applied and Environmental Microbiology*, **56**, 156-161.

KIENE, R.P. & TAYLOR, B.F. 1988a. Biotransformations of organosulphur compounds via 3-mercaptopropionate. *Nature*, **332**, 148-150.

KIENE, R.P. & TAYLOR, B.F. 1988b. Demethylation of dimethylsulphoniopropionate and production of thiols in anoxic marine sediments. *Applied and Environmental Microbiology*, **54**, 2208-2212.

KING, E.W. & EVERITT, D.A. 1980. A remote sampling device for under-ice water, bottom biota, and sediments. *Limnology and Oceanography*, **25**, 935–938.

KOHNEN, M.E.L., SINNINGHE DAMSTE', J.S., TEN HAVE, H.L. & DE LEEUW, J.W. 1989. Early incorporation of polysulphides in sedimentary organic matter. *Nature*, **341**, 640-641.

LASKIN, A.I. & LECHEVALIER, H.A. 1984. *CRC Handbook of Microbiology, 2nd Edition. Volume VII, Microbial Transformation*. Boca Bata: CRC Press, 606 pp.

LOVELOCK, J.E. 1974. CS_2 and the natural sulphur cycle. *Nature*, **248**, 625-626.

LOVELOCK, J.E. & MAGGS, R.J. & RASMUSSEN, R.A. 1972. Atmospheric dimethyl sulphide and the natural sulphur cycle. *Nature*, **237**, 452-453.

MARUYAMA, F.I. 1970. Identification of dimethyl trisulphide as a major aroma component of cooked brassicaceous vegetables. *Journal of Food Science*, **35**, 540-543.

MCMILLAN, F.H. & KING, J.A. 1948. Studies on the Willgerodt reaction. VI. A mechanism for the primary thiol oxidation. *Journal of the American Chemical Society*, **70**, 4143-4150.

MILLER, A., SCANLAN, R.A., LEE, J.S., LIBBEY, L.M. & MORGAN, M.E. 1973. Volatile compounds produced in sterile fish muscle (*Sebastes melanops*) by *Pseudomonas perolens*. *Applied Microbiology*, **25**, 257-261.

PICKERING, T.L., SAUNDERS, K.J. & TOBOLSKY, A.V. 1967. Disproportionation of organic polysulphides. *Journal of the American Chemical Society*, **89**, 2364-2367.

ROBERTS, N.J. 1991. *In Annual Report to the Australian Antarctic Division.* Kingston: Australian Antarctic Division, 181 pp.

ROBERTS, N.J. & BURTON, H.R. 1993. Sampling volatile organics from a meromictic Antarctic lake. *Polar Biology*, **13**, 359-361.

STEUDLER, P.A. & PETERSON, B.J. 1984. Contribution of gaseous sulphur from salt marshes to the global sulphur cycle. *Nature*, **311**, 455-457.

TARBELL, D.S. 1961. The mechanisms of oxidation of thiols to disulphides. *In* KHARASCH, N. *ed. Organic Sulphur Compounds*. Volume I. Oxford: Permagon Press, 97-102.

VAN DEN HOFF, J. & FRANZMANN, P.D. 1986. A choanoflagellate in a hypersaline Antarctic lake. *Polar Biology*, **6**, 71-73.

VICENTE, C. 1991. Biochemical and environmental influence on the synthesis and accumulation of lichen phenolics. *Lichen Biology*, **11**, 279-297.

WAJON, J.E., ALEXANDER, R. & KAGI, R.I. 1985. Determinations of trace levels of dimethyl polysulphides by capillary gas chromatography. *Journal of Chromatography*, **319**, 187-194.

WAJON, J.E. & WILMOT, P.D. 1992. Sulphur compounds causing odour in water. *Chemistry in Australia*, **59**, 28-30.

WAKEHAM, S.G., HOWES, B.L. & DACEY, J.W.H. 1984. Dimethyl sulphide in a stratified coastal salt pond. *Nature*, **310**, 770-772.

WAKEHAM, S.G., HOWES, B.L., DACEY, J.W.H., SCHWARZENBACK, R.P. & ZEYER, J. 1987. Biogeochemistry of dimethylsulphide in a seasonally stratified coastal salt pond. *Geochimica et Cosmochimica Acta*, **51**, 1675-1684.

WHITE, R.H. 1982. Analysis of dimethyl sulphonium compounds in marine algae. *Journal of Marine Research*, **40**, 529-536.

ZEHNDER, A.J.B. & ZINDER, S.H. 1980. The sulphur cycle. *In* HUTZINGER, O. *ed. The Handbook of Environmental Chemistry. Volume 1 Part A. The natural environmental and the biogeochemical cycles*. Berlin, Heidelberg: Springer-Verlag, 105-144.