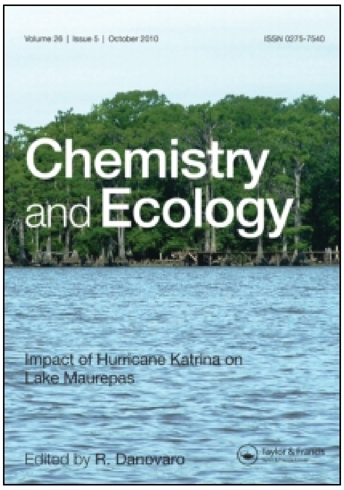

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DIMETHYLSULPHIDE AND OCEAN–ATMOSPHERE INTERACTIONS

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Dimethylsulphide (DMS) is a trace sulphur gas found in most atmospheric and surface water samples, which is derived from dimethylsulphonioproprionate (DMSP). Although it has been extensively studied over the last 50 years, its natural production, consumption and cycling are still not completely understood. Until recently, DMS was believed to originate mainly from marine waters, but later studies have shown that estuaries and lakes are also an important source of DMS. DMS also originates from terrestrial plants such as maize, wheat and lichen, but it is not fully understood why. DMS is believed to have an important impact on the global environment by influencing factors such as the acidity of the atmosphere, cloud condensation nuclei (CNN) and solar insolation. The impact that humans have on the cycling of DMS and on its environmental impact is not well understood either. DMS is affected by temporal and geographical factors, as well as physical factors such as salinity and wind speed, yet when studied under El Niño conditions which modify these physical factors *in vivo*, there was found to be no fluctuation in the concentration of DMS in the water column. This review outlines our current state of knowledge on DMS.

Keywords: DMS; Fluxes; Concentration; Ocean; Atmosphere

1 INTRODUCTION

DMS is a component of the atmospheric global sulphur cycle that is derived from DMSP, an organic osmolyte that acts as a compatible solute in algal cells (Malin and Kirst, 1997). DMS has been the subject of several studies, especially following the theory proposed by Charlson *et al.* (1987) that DMS and its oxidation products are important in atmospheric chemistry and global warming. This is because these compounds act as sulphur carriers from the oceans; contribute to the acidity of the atmosphere and become a source of new particles, which may affect the radiation balance of the atmosphere (Charlson *et al.*, 1987). Although several studies have been done, none of them have confirmed or disapproved completely of this theory, nor has the cycling of DMS or its impact on the environment been completely understood. This paper presents an up-to-the-moment review of the known literature and summarizes our state of knowledge.

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1.1 What is Dimethylsulphide (DMS)?

Dimethylsulphide (CH_3SCH_3; Fig. 1) is the smallest member of the dialkyl sulphides or aliphatic thioethers (Martin and Hauthal, 1971; Schöberl and Wagner, 1995). DMS is a trace sulphur gas found in most atmospheric and surface water samples (Turner and Liss, 1985; Kim and Andreae, 1987) and is the dominant volatile sulphur compound present in marine surface waters (Barnard *et al.*, 1982; Andreae and Raemdonck, 1983). This compound accounts for more than 95% of the observed reduced sulphur in surface ocean waters (Cline and Bates, 1983), and it is considered to be the major source of sulphate aerosols in the marine troposphere (Bonsang *et al.*, 1980). On the basis of its concentration and turnover, DMS is one of the most important biogenic sulphur compounds in the marine environment. It accounts for >50% of the total biogenic sulphur entering the atmosphere annually, and approximately 90% of this DMS originates from marine sources (Andreae, 1990).

Estimates of the size of the total global DMS budget range from 15 to 109 Tg per annum (Erickson III *et al.*, 1990; Schlesinger, 1996). The main reasons for this large range are differences in the way that the marine portion, which is the largest part of the budget, is calculated (Holligan *et al.*, 1987). One approach involves the use of the measured seawater concentrations and a mass transfer coefficient (Liss and Slater, 1974); another is to base the flux estimate on atmospheric concentrations and residence times (Wanninkhof, 1992). The concentrations are also affected by the composition of the marine water micro-layer which itself is not well understood (Yang *et al.*, 2001).

DMS is produced by enzymatic cleavage of DMSP, its precursor compound, which is released by marine phytoplankton in the upper ocean and acts as a compatible solute in algal cells (Malin and Kirst, 1997; Gabric *et al.*, 2001). This is believed to be the most dominant pathway for the production of DMS in saline environment (Andreae *et al.*, 1983; Andreae and Raemdonck, 1983; Ginzburg *et al.*, 1998). DMS is also produced during chemical and biological metabolism of other methylated sulphur compounds like *S*-methylcysteine, syringate, dimethylsulphoxide (DMSO), methylmercaptan (CH_3SH) and dimethyldisulphide (DMDS; Kiene, 1988; Finster *et al.*, 1990).

After ventilation to the atmosphere, DMS is oxidized to form sulphate aerosols, which, in the unpolluted marine atmosphere, are a major source of cloud condensation nuclei (CCN; Gabric *et al.*, 2001). Therefore, DMS has the potential to influence the radiative balance and global climate patterns (Simó and Pedrós-Alió, 1999a).

1.2 Dimethylsulphonioproprionate (DMSP)

The existence of DMS in the environment is the result of a complex set of biochemical reactions (Groene, 1995). The main precursor of DMS is DMSP ($[CH3]_2S^+CH_2CH_2COOH$; Fig. 2), which is similar in structure to the betaines (Cantoni and Anderson, 1956; Blunden and Gordon, 1986; Kiene and Taylor, 1988).

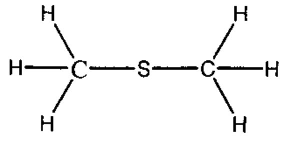

FIGURE 1 DMS structure.

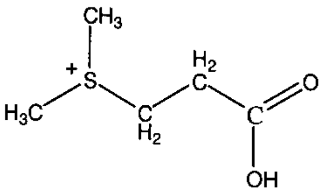

FIGURE 2 DMSP structure.

DMSP is an abundant osmo-protectant produced and stored by marine phytoplankton, macroalgae, cyanobacteria and coastal vascular plants (e.g. *Spartina alterniflora*). It can be metabolized to DMS and acrylate by microbes using the enzyme DMSP lyase (Reed, 1983; Vairavamurthy *et al.*, 1985; Dickson and Kirst, 1986; Dacey *et al.*, 1987; Gröne and Kirst, 1992; Baumann *et al.*, 1994; Ansede *et al.*, 2001). To protect their cells from dehydration (due to osmotic pressure), it is thought that marine algae produce the zwitterion molecule (DMSP) to act as an internal osmotic pressure regulator (Vairavamurthy *et al.*, 1985). DMSP is released continuously by living algae, as well as when algal walls are ruptured by copepod grazing, senescence or decay following bloom conditions, releasing the intracellular DMSP into the water column or sediment (Vairavamurthy *et al.*, 1985; Dacey and Wakeham, 1986; Belviso *et al.*, 1990; 1993; Wolfe *et al.*, 1994; Nguyen *et al.*, 1998). DMSP is then converted to DMS by cleavage of the secondary S—C bond, also releasing acrylic acid (Kelly and Smith, 1990). Kwint *et al.* (1996) showed that the DMS release or production was not necessarily associated with the death of phytoplankton after a bloom (Kwint and Kramer, 1995; Kwint *et al.*, 1996). The enzymatic degradation of DMSP to DMS and acrylate has been observed in marine and estuarine bacteria, fungi and algae under several different physico-chemical conditions (Dacey and Wakeham, 1986; Kiene and Visscher, 1987; Kiene, 1990; Stefels and van Boekel, 1993; Suzuki *et al.*, 1997). DMSP is an insoluble gas and is, therefore, degassed to the atmosphere rapidly. While in solution, it may also undergo photo-oxidation to form dimethylsulphoxide (DMSO) (Brimblecombe and Shooter, 1986).

1.3 Dimethylsulphoxide (DMSO)

Bacterial oxidation and photo-oxidation of DMS lead to the formation of DMSO (Brimblecombe and Shooter, 1986). In return, DMSO can be reduced to DMS by marine bacteria (Zinder and Brock, 1987; Jonkers *et al.*, 1996). New results indicate that DMSO in aquatic environments can act as a significant source of DMS rather than a sink (de Mora *et al.*, 1996; Simó *et al.*, 1999). DMSO is known to be a product from the addition channel of the OH/DMS reaction. This has been shown in laboratory investigations (Sørensen *et al.*, 1996), but it has also been measured in field studies (Berresheim *et al.*, 1993; 1998).

2 SAMPLING

2.1 Atmospheric

One of the techniques used for the collection and analysis of atmospheric DMS is described by Lee *et al.* (1999), in which air is drawn into trapping (absorption) tubes from a height of

2 m above the surface. If the samples are stored under dark conditions, the analysis can be done within 2–3 d of their collection without any detectable loss of DMS (Putaud *et al.*, 1999; Kim *et al.*, 2000). Another method is to collect the samples with pressuring electropolished stainless steel sample bottles with air pumped from the main Pyrex glass manifold using a metal bellows pump (Allan *et al.*, 1999).

2.2 In the Water Column

Water samples have been collected using 5-l Niskin bottles, the ship's biological pumping system, the ship's sea chest, or a polyvinyl chloride bucket. No significant differences in DMS concentration were found when using various sampling methods (Bates *et al.*, 1987). A distinction can also be made between the sampling sources. In this case, surface water samples were collected using lead-weighted glass bottles that were completely filled to the brim and tightly sealed with Teflon-coated caps (Pio *et al.*, 1996; Cerqueira and Pio, 1999). In comparison with the surface seawater, the microlayer has so far received little attention as regards the distribution of DMS and its influencing factors (Yang *et al.*, 2001), although Nguyen *et al.* (1978) among others found enriched DMS in the microlayer (Nguyen *et al.*, 1978; Yang, 1999). Another often-used method involves a gas-stripping method to concentrate the DMS samples (Kwint and Kramer, 1995) followed by an analysis of the DMS according to Lindqvist (1989) on a gas chromatograph equipped with a capillary linear PLOT column and a photo-ionization detector with hydrogen as the carrier gas (Lindqvist, 1989; Kwint and Kramer, 1995; Kwint *et al.*, 1996). DMS can also be analysed by sulphur-specific gas chromatography where it is measured in unfiltered seawater (Leylard and Dacey, 1996).

3 CYCLING OF DIMETHYLSULPHIDE

Sulphur is taken up by plants and algae and then reduced to form organosulphur compounds. Marine algae produce DMSP, which has an osmoregulating function but may also be enzymatically cleaved to yield the volatile DMS (Dickson *et al.*, 1980; Andreae, 1990). DMS is released from the water column via an air–sea exchange and converts oxidatively into stable end-products including non-sea salt sulphate (nss SO_4^{2-}), methane sulphonate (MSA) and dimethylsulphone (Kiene and Bates, 1990; Berresheim and Eisele, 1997). These end-products are capable of incorporating into the CNN, which in turn can affect the cloud albedo as a function of cloud droplet size (Berresheim *et al.*, 1998). Before being released into the atmosphere, some part of DMS may be oxidized by bacteria (Kiene and Bates, 1990). DMS is a dominant fraction of the natural oceanic emissions and accounts for most of the non-sea salt sulphate in the atmosphere above the remote open oceans (Bates *et al.*, 1992).

The amount of DMS released into the atmosphere is estimated at $12–58 \times 10^6\ \mathrm{t\ yr^{-1}}$ (Lelieveld *et al.*, 1997). Because of its biological origin, DMS is normally restricted to the upper 200 m of the water column with maximum concentrations near the bottom of the mixed layer (Cline and Bates, 1983; Andreae and Barnard, 1984). Below this maximum, the concentration decreases exponentially with near-zero concentrations ($<10\ \mathrm{pmol\ l^{-1}}$) at 200 m. The surface layers are always observed to be supersaturated with DMS, implying a net flux to the atmosphere (Barnard *et al.*, 1982; Andreae and Raemdonck, 1983). Its concentration in the oceans is believed to be regulated by a complicated interplay of algal speciation and trophic interactions (Andreae, 1990). DMS has a diurnal cycle attributed to

TABLE I DMS concentrations in sea water and marine atmosphere and fluxes (from marine water to the atmosphere) from the literature (units have been kept in their original published form).

	Concentration		*Flux*	
Location	*Mean*	*Range*	*Global estimates (Tg yr^{-1}/ Tmol S yr^{-1})* *Local estimates (nmol m^{-2} h^{-1})*	*Reference*
Oceanic				
Atmosphere				
Antarctica	806 ± 300 ng m^{-3}		5.8 ± 2.2 Tg yr^{-1}	Wylie *et al.*, 1991
Atlantic Ocean	422 ± 329 ng m^{-3}		15.6 ± 12.3 Tg yr^{-1}	Andreae *et al.*, 1985
Atlantic Ocean North	97 ng S m^{-3}	2–411 ng S m^{-3}		Andreae *et al.*, 1985
Bahamas	122 ng S m^{-3}	5–670 ng S m^{-3}		Andreae *et al.*, 1985
Equatorial Pacific	156 ± 36 ng m^{-3}		2.9 ± 0.7 Tg yr^{-1}	Andreae and Raemdonck, 1983
Equatorial Pacific	108 ± 10 ng m^{-3}		1.7 ± 0.2 Tg yr^{-1}	Bandy *et al.*, 1993a,b
Equatorial Pacific	301 ± 78 ng m^{-3}		6.5 ± 1.8 Tg yr^{-1}	Andreae *et al.*, 1985
Halley Bay (east Weddell Sea)	102 ng S m^{-3}	3.9–714 ng S m^{-3}		Davison *et al.*, 1996
North Atlantic	122 ± 122 ng m^{-3}		1.9 ± 1.9 Tg yr^{-1}	Johnson and Bates, 1993
North Atlantic	152 ± 81 ng m^{-3}		3.2 ± 1.7 Tg yr^{-1}	Andreae *et al.*, 1985
North Pacific	47 ± 25 ng m^{-3}		1.7 ± 0.9 Tg yr^{-1}	Andreae *et al.*, 1988
Sargasso Sea	232 ng S m^{-3}	1–1014 ng S m^{-3}		Andreae *et al.*, 1985
South Pacific	335 ± 99 ng m^{-3}		7.2 ± 2.3 Tg yr^{-1}	Andreae *et al.*, 1985
South of Falkland Islands (in air)	73 ng S m^{-3}	<0.1–714 ng S m^{-3}		Davison *et al.*, 1996
Tropical Atlantic	125 ± 56 ng m^{-3}		3.5 ± 1.6 Tg yr^{-1}	Johnson and Bates, 1993
Tropical Atlantic	177 ± 50 ng m^{-3}		6.6 ± 2.0 Tg yr^{-1}	Andreae *et al.*, 1985
Tropical Atlantic	213 ± 43 ng m^{-3}		6.9 ± 1.6 Tg yr^{-1}	Gregory *et al.*, 1986
Tropical Atlantic	248 ± 120 ng m^{-3}		9.2 ± 4.5 Tg yr^{-1}	Putaud *et al.*, 1992
Tropical Pacific	248 ± 136 ng m^{-3}		9.2 ± 5.1 Tg yr^{-1}	Nguyen *et al.*, 1984
Water				
Arctic Ocean	830 ± 800 ng m^{-3}		5.9 ± 5.8 Tg yr^{-1}	Hobbs *et al.*, 1992
Atlantic Ocean south of the Azores Islands	0.82 nmol l^{-1}		49 nmol m^{-2} h^{-1}	Putaud and Nguyen, 1996
Atlantic Ocean Northeast	12 nmol S l^{-1}	1.06–93.8 nmol S l^{-1}	721 nmol m^{-2} h^{-1}	Malin *et al.*, 1993
Baltic Sea		0.06–6.24 nmol S l^{-1}		Leck *et al.*, 1990
Equatorial Atlantic	213 ± 43 ng m^{-3}		6.9 ± 1.6 Tg yr^{-1}	Gregory *et al.*, 1986
Grand banks	0.3 nM			Scarratt *et al.*, 2000
Gulf stream	0.3 nM			Scarratt *et al.*, 2000

(*continued*)

TABLE I Continued.

	Concentration		*Flux*	
Location	*Mean*	*Range*	*Global estimates (Tg yr^{-1}/ Tmol S yr^{-1}) Local estimates (nmol m^{-2} h^{-1})*	*Reference*
Gulf of Mexico		0.2–5.1 nM		Kiene and Linn, 2000
Indian Ocean off the coast of Australia		ND–6.0 nM		Curran *et al.*, 1998
Indian Ocean off the coast of Australia		0.4–6.8 nM		de Bruyn *et al.*, 1998
Indian Ocean off the coast of Australia		ND–5.6 nM		Jones *et al.*, 1998
Indian Ocean off the coast of Australia		0.8–28 nM		McTaggart and Burton, 1992
Labrador Basin		1.7–11.8 nmol l^{-1}		Schultes *et al.*, 2000
Ligurian Sea	4.6 nmol S l^{-1}			Belviso *et al.*, 1993
Mediterranean Sea Western	1.8 nmol S l^{-1}	0.1–4.3 nmol S l^{-1}		Simó *et al.*, 1997
North Atlantic	112 ± 20 ng m^{-3}		2.3 ± 0.5 Tg yr^{-1}	Hewitt and Davison, 1997
North Atlantic drift	2.3 nM			Scarratt *et al.*, 2000
Pacific Ocean Northeastern	4.1 nmol S	1.54–10.82 nmol S		Watanabe *et al.*, 1995
Pacific Ocean		0.31–90.63 nmol S		Bates *et al.*, 1987
Sargasso Sea		0.4–2.1 nM		Ledyard and Dacey, 1996
Sargasso Sea	2.2 nM			Scarratt *et al.*, 2000
South Pacific	41 ± 9 ng m^{-3}		0.1 ± 0.02 Tg yr^{-1}	Harvey *et al.*, 1992
Vineyard Sound		2.3–5.6 nM		Ledyard and Dacey, 1996
World oceans	3.0 nmol l^{-1}		0.6–1.7 (Tmol S yr^{-1})	Andreae, 1990
Coastal and shelf regions				
Atmosphere				
Antarctic Peninsula	44 ng S m^{-3}	9.37–204 ng S m^{-3}		Davison *et al.*, 1996
Cape Grim, Tasmania	167 ng S m^{-3}	34–481 ng S m^{-3}		Andreae *et al.*, 1985
Cheju Island Korea		19–1140 pptv		Kim *et al.*, 2000
North-west USA	207 ± 194 ng m^{-3}		1.6 ± 1.5 Tg yr^{-1}	Berresheim *et al.*, 1993
North-west USA	69 ± 19 ng m^{-3}		1.4 ± 0.4 Tg yr^{-1}	Berresheim *et al.*, 1993
North-west USA	136 ± 37 ng m^{-3}		1.7 ± 0.5 Tg yr^{-1}	Andreae *et al.*, 1988
Water				
Brittany, France	41 ± 40 ng m^{-3}		0.5 ± 0.5 Tg yr^{-1}	Nguyen *et al.*, 1983
Brittany, France	868 ± 372 ng m^{-3}		10.6 ± 4.6 Tg yr^{-1}	Watts, 2000
Brittany, France	1581 ± 1556 ng m^{-3}		31.5 ± 31.2 Tg yr^{-1}	Putaud *et al.*, 1999

Brittany, France	1085 ± 620 ng m^{-3}		21.6 ± 12.5 Tg yr^{-1}	Putaud *et al.*, 1999
Canal de Mira Portugal	2.9 (winter)–5.3 (summer) nmol l^{-1}		5.4 (winter)–27.3 (summer) nmol m^{-2} h^{-1}	Cerqueira and Pio, 1999
Coastal and shelf regions	2.8 nmol l^{-1}		0.6–1.7 (Tmol S yr^{-1})	Andreae, 1990
Gulf of Mexico		0.8–2.9 nM		Kiene and Linn, 2000
Gulf of St. Lawrence, east coast of Canada	3.0 (summer) nmol l^{-1}		196 (summer) nmol m^{-2} h^{-1}	Levasseur *et al.* 1997
Ligurian, coastal	16.2 nmol S l^{-1}			Boniforti *et al.*, 1993
Mediterranean Sea Coastal Western	4.9 nmol S l^{-1}	0.0–19.3 nmol S l^{-1}		Simó *et al.*, 1997
North Sea	2.1 (summer) nmol l^{-1}		768 nmol m^{-2} h^{-1}	Leck and Rodhe, 1991
North Sea	0.7 (winter)–7.5 (summer) nmol l^{-1}		73.3 (winter)–247 (summer) nmol m^{-2} h^{-1}	Turner *et al.*, 1996
Seawater around mainland Britain	0.12 (winter)–6.86 (summer) nmol S l^{-1}	0.03–34.31 nmol S l^{-1}		Turner *et al.*, 1988
Seas surrounding Britain	0.1 (winter)–6.9 (summer) nmol l^{-1}		20.8 (winter)–1217 (summer) nmol m^{-2} h^{-1}	Turner *et al.*, 1988
Venice lagoon		0.85–16.3 nmol S l^{-1}		Moret *et al.*, 2000
Others				
Atmosphere				
UK to Antarctica	54 ng S m^{-3}	0–714 ng S m^{-3}		Davison *et al.*, 1996
UK to Falkland Islands	18 ng S m^{-3}	2.8–47 ng S m^{-3}		Davison *et al.*, 1996
Water				
Upwelling (coastal and equatorial regions)	4.9 nmol l^{-1}		0.2–0.7 Tmol S yr^{-1}	Andreae, 1990
Temperate regions	2.1 nmol l^{-1}		0.1–0.3 Tmol S yr^{-1}	Andreae, 1990
Titanic NW Atlantic	1.0 nM			Scarratt *et al.*, 2000
Tropical and low-productivity regions	2.4 nmol l^{-1}		0.2–0.6 Tmol S yr^{-1}	Andreae, 1990

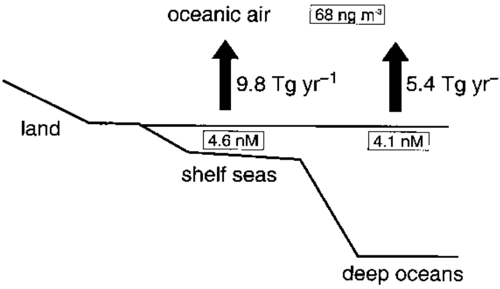

FIGURE 3 Schematic diagram of the mean concentrations of DMS in the oceanic and coastal waters, the flux to the atmosphere and the concentration in the maritime air. Flux values are calculated from the tabulated data above. The areal aspect of the flux has been preserved in making the calculation.

the rapid oxidation and removal of DMS by reactions with photochemically produced hydroxyl radical (OH); in clean air, concentrations of OH follow a strong diurnal pattern, with essentially zero concentrations during the hours of darkness (Logan *et al.*, 1981). In maritime influenced air masses, DMS concentrations are generally higher than in continental air due to a lack of sources and an increase in oxidant concentrations (Davison *et al.*, 1996). In addition to this, DMS and DMSP are rapidly cycled in the water column due to the bacterial activity, with the flux of DMS to the atmosphere being highly dependent on factors other than the production of cellular DMSP by phytoplankton alone (Kwint *et al.*, 1996). Until recently, DMS formation was found exclusively in saline waters and, therefore, was regarded as insignificant in freshwater. Several recent studies revealed that this process can be dominant in freshwater as well and that its product can affect the odour quality of some drinking and recreational water systems (Ginzburg *et al.*, 1998).

Estimates of the global sulphur emissions to the atmosphere show that 0.47–2.2 Tmol S yr^{-1} originate from natural sources, while 1.9–2.7 Tmol S yr^{-1} are of anthropogenic origin. About 66% of natural sulphur emissions are accounted for by DMS, with a range of 0.3–1.6 Tmol S yr^{-1} (Aneja, 1990; Rodhe, 1999). Hydrogen sulphide and DMS seem quantitatively to be the most important sulphur gases in coastal marine environments (Steudler and Peterson, 1984).

Table I presents a listing of the mean DMS concentrations, their ranges and fluxes from a series of marine measurements. The mean data have been used, where appropriate, to generate a schematic figure showing the mean concentrations and fluxes in the marine environment (Fig. 3).

4 SOURCES, SINKS AND FLUCTUATIONS

4.1 Sources

Natural sources of DMS are soils and plants, coastal wetlands and oceans (and as a gas (Andreae, 1990)). DMS may be produced directly from phytoplankton cells and algal cells or released when phytoplankton are subject to zooplankton grazing or bacterial attack and digestion by zooplankton, or finally by bacterial transformation of algal-derived DMSP (Cantoni and Anderson, 1956; Vairavamurthy *et al.*, 1985; Dacey and Wakeham, 1986). DMS can also be produced in the sediment from degradation of detritus settled on the bottom of the water column (Andreae, 1985).

It is generally considered that DMS concentrations in seawater are not closely associated with phytoplankton biomass, although some correlations were sometimes found between oceanic DMS concentrations and chlorophyll *a* (Andreae and Barnard, 1984; Barnard *et al.*, 1984; Andreae, 1990; Yang *et al.*, 1999; Yang, 2000). Some micro-organisms, such as the phototrophic purple bacteria, can generate DMS by reducing DMSO, though DMSO is considered to be the dead-end metabolite in these micro-organisms (Zinder and Brock, 1978; Jonkers *et al.*, 1996).

There are some reports of anoxygenic phototrophic bacteria able to oxidize DMS photo- or chemo-trophically to DMSO (Zeyer *et al.*, 1987; Visscher and van Gemerden, 1991; Hanlon *et al.*, 1994; Kelly *et al.*, 1994; Horinouchi *et al.*, 1999). Most of the DMS-oxidizing phototrophs described are tolerant to high concentrations of sulphide, indicating that these bacteria can reduce DMS emission rates in sulphidic environments (Vogt *et al.*, 1997). Several studies showed that *Thiocapsa roseopersicina*, an alga, is involved in the turnover of DMS and DMSP (Jonkers *et al.*, 1999). Dacey *et al.* (1987) suggested that *Spartina alterniflora* from salt marshes represents a considerable DMS source because of the high DMSP concentrations within the plants, whereas uncovered sediment areas showed only small DMS emissions or were DMS sinks (Dacey *et al.*, 1987). In addition, Kiene (1988) showed DMS emission from sediment cores only after inhibition of bacterial DMS consumption and concluded that the biological DMS consumption is the main sink for the DMS produced within the sediment (Kiene, 1988). Another example is that oceanic regions dominated by *Phaeocystis pouchetii*, a significant producer of DMS, have high concentrations of DMS (Barnard *et al.*, 1984; Malin *et al.*, 1992; Turner *et al.*, 1995). In the water microlayer, the most likely sources of DMS are *in-situ* production of phytoneuston and vertical export by turbulent diffusion from the underlying water. The mean production rate of DMS in the microlayer is more than twice that in the subsurface water (Yang *et al.*, 2001).

4.2 Sinks

The dominant sink for DMS and DMSP in seawater is thought to be biological (bacterial consumption, microbial degradation), but simple physico-chemical processes may be active: ventilation into the atmosphere (air-to-sea exchange) and photochemical oxidation of DMS (Brimblecombe and Shooter, 1986; Wolfe and Kiene, 1993; Osinga *et al.*, 1996; Malin and Kirst, 1997).

Research has suggested that microbial consumption was the most important sink for seawater DMS (Kiene and Bates, 1990; Wolfe and Kiene, 1993; Simó and Pedrós-Alió, 1999b). Although the total amount of DMS entering the atmosphere from the ocean is significant on a global scale, the sea-to-air emission may represent only a minor sink for seawater DMS (Bates *et al.*, 1994). Recent work indicated that the photochemical oxidation of DMS, to DMSO or other products, accounts for only 7–40% of the total removal of DMS from the surface mixed layer (Kieber *et al.*, 1996). In contrast, Brugger *et al.* (1998) found that 88% of the DMS was photolysed in the top 10 m of the water column (Brugger *et al.*, 1998). Recent studies indicate that halogen atoms and halogen oxides may also be important sinks of DMS (Pszenny *et al.*, 1993; George *et al.*, 1994; Toumi, 1994).

The main sink for DMS in the atmosphere is its reaction with OH by day and NO_3 by night (Wilson and Hirst, 1996; Watts, 2000). The OH reaction can be either an abstraction or an addition reaction: effectively, the two paths compete. However, only at low temperatures (<300 K, temperate winter) is the addition reaction the major pathway (Wilson and Hirst, 1996). The NO_3 reaction is an abstraction, with a reaction rate that is of the same order as the OH abstraction. Kinetic studies indicate residence times of DMS in the atmosphere between 24 and 28 h dependent on atmospheric composition and temperature (Barnes *et al.*, 1988; 1994).

4.3 Fluctuations

Fluctuations in the DMS concentration seem to be generated by several factors. These factors are often noticed in trends found during sampling. DMS is the only gaseous sulphur compound which frequently showed a dependency on the tidal cycle with higher emission rates at the beginning of the ebb tide and lower values at the end (Bodenbender *et al.*, 1999). Well-drained tidally flooded sites seem to produce much more DMS than similar sites with poorer drainage (Hines *et al.*, 1993). In addition to this, upwelling deeper ocean water appears to have the highest mean DMS concentration because of elevated phytoplankton levels in colder and more nutrient-rich water (Andreae *et al.*, 1994), and the mixing-layer depths (which are driven by climate) have a substantial influence on DMS yield on short timescales (Simó and Pedrós-Alió, 1999a). Baumann *et al.* (1994) showed a clear temperature dependency of DMS emissions by phytoplankton (Baumann *et al.*, 1994). This substantiates early statements that emissions of DMS by phytoplankton are related to physiological stress (Kirst *et al.*, 1991; Nguyen *et al.*, 1998).

DMS can also be produced in the sediment by degradation of detritus settled at the bottom of the water column (Andreae, 1985). Laboratory experiments with relatively undisturbed sediment cores showed that microbial mats act as sinks for DMS under oxic/light (day) conditions and as a source of DMS under anoxic/dark (night) conditions (Jonkers *et al.*, 1998). DMS emissions from intact microbial mats incubated under oxic/light conditions were below the detection limit ($<19\ \mathrm{nmol\ m^{-2}\ h^{-1}}$), and under anoxic/dark conditions, emissions rates were $632 \pm 241\ \mathrm{nmol\ m^{-2}\ h^{-1}}$ (Jonkers *et al.*, 1998). The loss of DMS from surface waters is due to bacterial oxidation, photolysis and efflux to the atmosphere (Brimblecombe and Shooter, 1986; Kiene, 1992; Kieber *et al.*, 1996).

Kwint and Kramer (1996) showed that between 30 and 50% of DMS in the air above the sea/air interface ventilates from the ocean during a 6-week window closely related to phytoplankton blooms. This correlates with the emerging idea that only in special circumstances does the DMS concentration rise above normal background concentration (Kwint and Kramer, 1996). More recently, van Duyl *et al.* (1998) and Wolfe *et al.* (1999) found that DMS consumption appeared to be tightly coupled with production (van Duyl *et al.*, 1998; Wolfe *et al.*, 1999). As might be expected, DMS emissions show strong seasonal and spatial variability, reflecting the seasonality of growth and patchy distribution of DMSP-producing marine phytoplankton (Malin and Kirst, 1997).

Abundant sources of DMSP are the various algal classes of phytoplankton as well as several benthic macroalgae. In typical phytoplankton species, high concentrations of DMSP are found in chlorophyll a/c algae (Dinophytes, Prymnesiophytes, some species of the Bacillariophytes and the Chrysophytes and some diatoms) and the chlorophyll a/b-containing Prasinophyceae (White, 1982; Reed, 1983; Dickson and Kirst, 1987a,b; Turner *et al.*, 1988; Keller *et al.*, 1989; Karsten *et al.*, 1990; Malin and Kirst, 1997). Its concentration depends on biotic and abiotic factors such as light, salinity, temperature, season, cell age, population density and composition (Reed, 1983; Vairavamurthy *et al.*, 1985; Dickson and Kirst, 1986, 1987a,b). However, it is important to note that fluxes reported in the literature are often obtained from summer values using a summer:winter ratio of 2.0–2.5; this would affect the seasonality factor differently (Moret *et al.*, 2000). DMS is accumulated with increasing salinity, together with other low-molecular-weight organic compounds (sugars, polyols, proline, etc.) and certain ions ($\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Cl^-}$), which balance changes in external osmotic potential (Kirst *et al.*, 1991).

Little is known about the spatial and temporal variation of bacterial DMS production and consumption on oceanic scales. In particular, there is a lack of knowledge about the variation of this activity as a function of temperature (Scarratt *et al.*, 2000). High concentrations of

DMS and DMSP can be found in areas of high algal productivity such as marine phytoplankton blooms (Malin and Kirst, 1997). Therefore, factors affecting the growth of bacteria such as grazing and nutrient limitations might also affect the relationship between DMSP turnover and bacterial production, thus affecting the amount of DMS produced (Kiene and Linn, 2000). Microbial processes and bacterial production and consumption have been established as both sources and sinks for DMS in seawater (Kiene and Bates, 1990; Kiene, 1992; Kwint and Kramer, 1995; Kwint *et al.*, 1996; Ledyard and Dacey, 1996; Wolfe *et al.*, 1999). However, there appears to be no direct correlation between chlorophyll *a* and DMS concentrations in oceanic surface waters (Dacey and Wakeham, 1986; Turner *et al.*, 1989; Bürgermeister *et al.*, 1990; Leck *et al.*, 1990).

The emission of DMS from terrestrial vegetation is also a little uncertain, due to the lack of data from temperate and boreal regions, but more from tropical forests (Fall *et al.*, 1988). Data are available for tropical forests (Gregory *et al.*, 1986; Andreae and Andreae, 1988; Jaeschke *et al.*, 1994), maize and wheat (Kanda *et al.*, 1995) and lichen (Gries *et al.*, 1994; Kuhn *et al.*, 1999). For other members of the terrestrial plant kingdom, data are lacking. However, quite apart from the fact that some plants do emit DMS, there is a large amount of circumstantial evidence that most vegetation is generally a source of DMS (Lovelock *et al.*, 1972).

Several studies indicate that the distribution of DMS in coastal environments can be subject to significant variability in both the temporal and spatial scales (Levasseur *et al.*, 1997; Kim *et al.*, 2000). However, Andreae *et al.* (1994) demonstrated that the enhancement of DMS emission rate could be due to physical factors such as wind speed and/or temperature. In addition to this, Yvon *et al.* (1996) and Warneke and de Gouw (2001) demonstrated and observed that atmospheric DMS exhibits a diel cycle. This was due to photolytic destruction by OH radicals, and therefore, the DMS concentrations during daytime periods were low relative to night-time periods (Yvon *et al.*, 1996; Warneke and de Gouw, 2001). In marine and estuarine systems, DMS is primarily derived from the degradation of DMSP (Kiene and Capone, 1988). In freshwater habitats, formation of DMS originates mainly from the methylation of sulphide and, to a lesser extent, from the degradation of sulphur-containing amino acids (Kadota and Ishida, 1972; Finster *et al.*, 1990; Kiene and Hines, 1995; Lomans *et al.*, 2001). Kirst *et al.* (1991) surveyed the ice algae in the Antarctic waters and revealed the highest concentrations of DMS and DMSP measured to date (Gibson *et al.*, 1990; Flogelqvist, 1991; Kirst *et al.*, 1991). Oligotrophic areas of the ocean typically have relatively low DMS and DMSP concentrations and display only modest seasonal variations (Kettle, 1999). Nevertheless, oligotrophic regions make up a large fraction of the worlds oceans and, therefore, contribute significantly to the global DMS flux to the atmosphere (Bates *et al.*, 1992). DMS concentrations in oligotrophic waters can reach concentrations of 5–12 nM (Dacey *et al.*, 1998).

The rate of DMS production depends directly on the concentration of DMS in surface waters, which is controlled by complex production and removal processes that are closely tied to the food web dynamics and physical factors such as air–sea exchange, water-column mixing and photochemistry (Dacey *et al.*, 1998). DMS emissions are dependent on the seawater DMS concentration and the air–sea exchange, which is determined mainly by the sea-surface temperature (SST) and the wind speed (McGillis *et al.*, 2000). The SST can influence the phytoplankton release of DMSP to the water (Watanabe *et al.*, 1995). Additionally, a lower SST generally would decrease the boundary layer height and increase the DMS mixing ratio, even at a constant emission. Therefore, the DMS mixing ratio is indirectly dependent on the SST. However, the gas-transfer velocity increases with temperature because the gas solubility decreases (McGillis *et al.*, 2000). Also, the net production of DMS is regulated by the activity of the DMSP-cleaving, DMSP-demethylating and DMS-oxidizing bacteria. This was shown by Jonkers *et al.* (2000), who observed a pronounced net production of DMS under anoxic/dark conditions and, in contrast, a minor net production under oxic/light conditions. However, the net production of DMS from DMSP is also affected by the competition for DMSP between the DMSP-cleaving and DMSP-demethylating organisms (Jonkers *et al.*, 2000).

5 MODELLING

One of the modelling methods used in evaluating the sea-to-air DMS fluxes is based on the mass-balance photochemical-modelling (MBPCM) approach. Saltzman and Cooper (1989), Thompson *et al.* (1990), Davidson and Hewitt (1992), Chen *et al.* (1999) and Davis *et al.* (1999) are some of the researchers who used this method. As outlined by Chen *et al.* (1999), to achieve the most reliable results using the MBPCM approach, the region under investigation must have (1) a reasonably high degree of surface DMS homogeneity and (2) gas-phase concentrations of DMS that reflect photochemical quasi-steady-state conditions. Given that the boundary layer is well mixed, the final form of the mass balance equation is as follows:

$$\frac{\mathrm{d}[DMS]}{\mathrm{d}t} = \frac{F_{DMS}}{EMD} - (k_{\mathrm{OH}}[\mathrm{OH}] + k_{\mathrm{NO_3}}[\mathrm{NO_3}])[DMS] + \frac{1}{EMD}\int_{hBL}^{hBUL} w\left(\frac{\partial[DMS(z)]}{\mathrm{d}z}\right)\mathrm{d}z.$$

Here, *EMD* defines the DMS Equivalent Mixing Depth, which can best be represented by:

$$EMD = \frac{\int [DMS(z)]\mathrm{d}z}{[DMS]_{BL}}.$$

In this equation, the quantity $[\mathrm{DMS}]_{\mathrm{BL}}$ represents the average concentration in the marine boundary layer (Chen *et al.*, 1999). After using the MBPCM model, Shon *et al.* (2001) suggested that further efforts should be made to incorporate the MBPCM flux approach with the sea-to-air gradient and other flux methods. This is in addition to selecting a favourable location where meteorological conditions are stable, and where DMS consequently has a short lifetime and a relatively uniform flux field (Shon *et al.*, 2001).

Another type of model is the two-layer model of Liss and Slater (1974) used by, among others, Putaud and Nguyen (1996), Levasseur *et al.* (1997) and Cerquiera and Pio (1999). It estimates the emission of DMS in the atmosphere by assuming that the flux (F) of the gas is proportional to the difference between the concentration in the surface water and the equilibrium solubility concentration:

$$F = K_{\mathrm{w}}(C_{\mathrm{w}} - C_{\mathrm{a}}H^{-1}),$$

where K_{w} is the transfer velocity, C_{a} and C_{w} are the gas concentrations in air and water, respectively, and H is the dimensionless Henry's law constant. As surface waters are highly supersaturated with DMS, C_{w} is much greater than the atmospheric concentration, and the term $C_{\mathrm{a}}H^{-1}$ is usually neglected. Therefore, the previous equation may be reduced to:

$$F = K_{\mathrm{w}}C_{\mathrm{w}}.$$

A third commonly used model is the Sulphur Box Model used by Chen *et al.* (2000). This consists of 14 reactions which collectively describe the sources and sinks for nine different sulphur species including DMS. The following equation shows the typical form that the differential equation would take in achieving a mass balance for some arbitrary sulphur species, S (e.g. DMS, DMSO or SO_2):

$$\frac{d[S]_{BL}}{dt} = \frac{F}{h} + \frac{M}{h}([S]_{BUL} - [S]_{BL}) + P(S) - L(S)[S]_{BL} - k_{SL}[S]_{BL}.$$

The first term on the right-hand side represents the oceanic source strength, where F is defined as the sea-to-air flux, and h is the marine boundary layer (BL) height, BUL is the buffer layer (the transition zone between BL and the free troposphere), and M is defined as $K/\Delta Z$ (with K as the mixing coefficient (Chen *et al.*, 2000)). Davis *et al.* (1996) and Crawford *et al.* (1999) are among many others who used the same model.

Several other models have been used, such as the compartment model for microbial mats. The model is based on biological production and consumption of organic carbon, DMS, hydrogen sulphide and oxygen (de Zwart and Kuenen, 1995; 1997), the box model of the chemistry in the boundary layer (Carslaw *et al.*, 1997; Allan *et al.*, 1999) and the atmospheric gas phase box model coupled to a three-mode integral aerosol dynamic. In this final case, the simulations show the dependency of the concentration of nucleation mode particles on initial pre-existing particles, the intensity of the UV radiation, the emissions of DMS and the ratio of emissions of hydrocarbons (HC) and NO_x present in the atmosphere (Pirjola and Kulmala, 1998). Finally, Prather *et al.* (1987) and Restad *et al.* (1998), among others, used a global 3D chemical tracer model (CTM). It is a hindcast model and uses 1 yr of meteorological data generated by the NASA-GISS GCM (Prather *et al.*, 1987; Restad *et al.*, 1998).

Unfortunately, there are some limitations to computer modelling of DMS, such as the exact concentration of DMS in the atmosphere, which cannot be determined using a computer model, as our current knowledge of DMS photochemistry is not at its full capacity, and therefore, dispersion and transportation must be included (Putaud *et al.*, 1999). In addition to this, accurate modelling of the biological DMS cycle in marine waters will require a dataset that charts the variations in relevant kinetic parameters on a seasonal basis (Ledyard and Dacey, 1996). However, some aspects of computer modelling are now considered as certainties. For example, a mass balance photochemical modelling approach can be used to evaluate the oceanic DMS flux; this method was previously used for other locations such as ground basis and airborne platforms (Saltzman and Cooper, 1989; Ayers *et al.*, 1995; Yvon *et al.*, 1996; Chen *et al.*, 1999; Davis *et al.*, 1999). A second certainty is that short-term kinetic incubations show that the potential community DMS production in the open ocean is a linear function of dissolved DMSP concentration and that it does not saturate. This finding is potentially useful for predictive modelling of oceanic DMS production (Scarratt *et al.*, 2000).

6 DMS AND THE CLIMATE

DMS emitted from the oceans is rapidly photo-oxidized to sulphur dioxide, methane sulphonic acid and sulphate aerosols that directly influence the earth's radiation budget by backscattering a part of the incoming solar radiation. The aerosols also serve as CNN and thereby increase the earth's albedo (Andreae *et al.*, 1995; Andreae and Crutzen, 1997). DMS and its oxidation products are important in atmospheric chemistry because they act as sulphur carriers from the oceans, contribute to the acidity of the atmosphere and act as a source for new particles, which may affect the radiation balance of the atmosphere (Charlson *et al.*, 1987). These atmospheric oxidation products are the major source of sub-micron aerosol particles over remote marine areas, and these aerosol particles influence the global climate directly by scattering and absorbing radiation and indirectly by affecting cloud albedo (Shaw, 1983; Charlson *et al.*, 1987; 1992).

The main radicals involved in the gas-phase atmospheric oxidation of DMS are OH^- and NO_3^- (Patroescu *et al.*, 1999). Furthermore, since oxidation products are mainly acidic, DMS influences the pH of aerosols and rain in remote areas, e.g. the Antarctica and the North Pacific as well as in lightly industrialized areas such as Ireland and Scandinavia (Wagenback *et al.*, 1988; Fletcher, 1989; Savoie and Prospero, 1989; Turner *et al.*, 1989). There is a net flux of DMS from the ocean to the atmosphere of the order of 15–45 Tg S yr^{-1} (Andreae, 1990; Bates *et al.*, 1994).

Several recent studies suggest that although emissions of anthropogenic sulphur dominate on a global scale, rapid deposition close to source areas means that biogenic sulphur may dominate the global sulphur burden (Malin and Kirst, 1997).

A study by Ayers *et al.* (1997) revealed that there was a clear seasonal relationship between atmospheric DMS, its atmospheric oxidation products (methanesulphonic acid or MSA, SO_2, and non-sea salt sulphate), the concentration of CNN and cloud optical depth (Ayers *et al.*, 1997). This concurs with the controversial suggestion made by Charlson *et al.* (1987) that the connection between DMSP-producing algae and clouds represented a climate-regulating mechanism (Charlson *et al.*, 1987). A schematic diagram indicating the feedback mechanism is shown in Fig. 4. According to this theory, warmer ocean

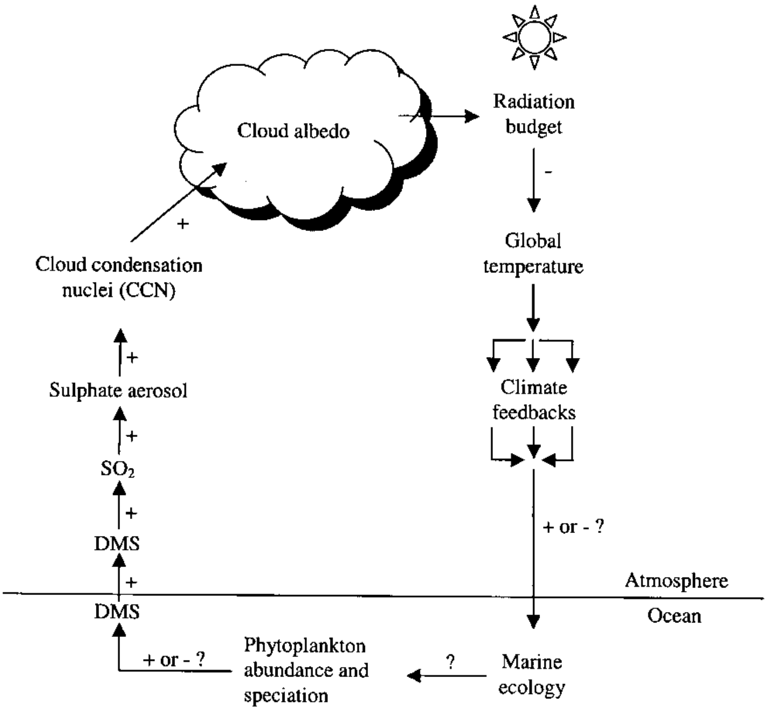

FIGURE 4 Proposed feedback cycle between the climate and marine DMS production. The pluses and minuses indicate whether an increase in the value of the preceding parameter in the cycle is expected to lead to an increase (+) or decrease (−) in the values of the subsequent parameter (after Andreae, 1990).

temperatures resulting from global climate warming would stimulate processes leading to the production of DMS. The enhanced DMS release would lead to increased formation of sulphate aerosols and CNN. Increased light scattering and cloud cover would exert a cooling effect on the climate, thereby counteracting the warmer trend. The existence of this "global thermostat" has not yet been confirmed but there is evidence to support a relationship between DMS-derived sulphate aerosols and climatic events (Falkowski *et al.*, 1992; Legrand, 1997; Legrand *et al.*, 1997; Clarke *et al.*, 1998), but the processes involved may be more complex than predicted by Charlson *et al.* (Malin and Kirst, 1997). Several authors postulated a regulatory effect of CNN on global warming (e.g. Ayers and Gras (1991) and Charlson *et al.* (1991)), but Bates and Quinn (1997) concluded that Charlson *et al.*'s (1987) hypothesized DMS-climate feedback link remains elusive. They sampled the equatorial Pacific Ocean and noticed that the large inter-annual variations in oceanic (sea-surface temperature, mixed layer depths and upwelling rates) and atmospheric (cloud cover and precipitation) properties were associated with ENSO (El Niño-Southern Oscillation) events. However, these changes had little effect on DMS concentrations in surface ocean waters (Bates and Quinn, 1997).

Apart from the emission strength of the ocean, the atmospheric DMS mixing ratio is a function of several parameters: the OH concentration, the boundary layer height and the vertical exchange between the boundary layer and the free troposphere (Bandy *et al.*, 1996). Fluxes of DMS to the atmosphere depend on the steady-state concentrations of these compounds in the sediment and the water surface layers. These steady-state concentrations are the result of biological and chemical production and degradation (Kiene *et al.*, 1986; Lomans *et al.*, 1997; 1999a,b).

7 DMS AND THE NATURAL MARINE ECOSYSTEM

DMS affects the natural marine ecosystems in at least three ways. Firstly, high concentrations of DMS are toxic and malodorous and can therefore lead to local environmental problems (de Zwart and Kuenen, 1992). Secondly, atmospheric oxidation products of DMS, as well as contributing to acid precipitation, act as precursors for CCN (Charlson and Rodhe, 1982). Therefore, they potentially contribute to cloud formation (Charlson *et al.*, 1987). Thirdly, DMS is quantitatively the most important compound involved in the transport of sulphur from oceanic to terrestrial areas (Lovelock *et al.*, 1972).

8 HUMAN IMPACT

Man's activity over the last 100–150 yr has perturbed the global sulphur cycle, especially in the northern hemisphere, which receives about 90% of the anthropogenic inputs to the atmosphere (Houghton *et al.*, 1996). Man-made emissions of sulphur are of the order of 93 ± 15 Tg S yr^{-1} (Jørgensen and Okholm-Hansen, 1985).

DMS can have a negative impact on the environment and on human health, as both the liquid and vapour form of DMS are harmful to the skin, eyes and mucous membranes (World Health Organization, 1989). There are no warning properties (no smell or initial irritation), and the symptoms are delayed by a few hours. Therefore, a UK maximum occupational exposure limit of 0.05 ppm of DMS related to an 8-h time weight average reference period has been set (Health and Safety Executive, 1997). DMS is used as a methylating agent in organic synthesis and the production of pharmaceuticals, and as a quaternizing agent in dyestuffs manufacture (Scobbie and Groves, 1998).

9 CONCLUSION

DMS, its cycling and its role in the environment or the atmosphere, as well as its sinks and sources, are still relatively poorly understood despite a considerable number of studies. One of the reasons might be that all the observations have been made taking different aspects into consideration. Another might be that DMS and all its components vary widely from one location, and therefore it is not practical to compare results from, say, the Atlantic with some of the Antarctic or an estuary. Also, most studies represent very short time periods with a high temporal variability in the concentrations leading to an apparently large spatial variation. Considering the proposed climate feedback that DMS may have on the earth's radiation budget by backscattering a part of the incoming solar radiation, effort still needs to be directed towards this small chemical molecule with large potential effects.

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