

Chapter 2

REVIEW OF LITERATURE

2.1 Introduction

In recent years, the knowledge about biogenic sulphur emissions from the oceans has considerably improved. Marine emissions of reduced sulphur gases are an essential element of the global sulphur cycle and the main source of biogenic sulphate aerosols, which play important roles in atmospheric chemistry and climate change. The main gases which are released from the ocean surface are dimethylsulphide (DMS), H_2S , carbon disulphide (CS_2), and carbonyl sulphide (COS).

DMS is a climatically important volatile sulfur compound produced by the biologically- and physically – mediated breakdown of dimethylsulphoniopropionate (DMSP), an organosulfur compound synthesized by oceanic phytoplankton (Fig. 1).

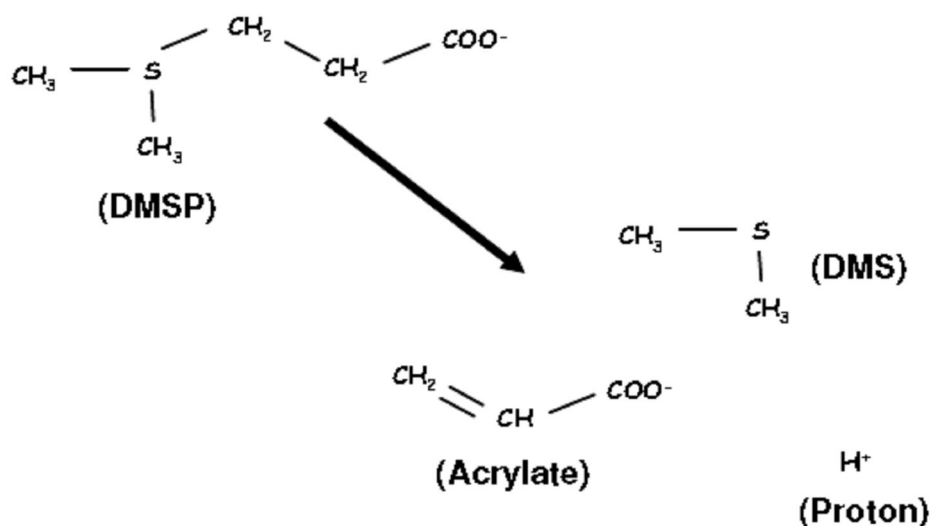


Fig. 1 DMSP cleavage to DMS, acrylate and a proton.

DMS is a radiatively important volatile biogenic sulfur compound in marine waters (Bates et al. 1987a). Its flux from the ocean to the atmosphere makes it a major contributor to the global sulfur cycle (Andrea et al. 1995). DMS is responsible for more than 95% and 20% of marine and global sulphur emissions, respectively. DMS is transferred across the air/sea interface by a combination of molecular and turbulent diffusion processes. Scientific interest in the DMS cycle heightened because of “CLAW” hypothesis put forward by Charlson et al. (1987) (“CLAW” comes from the first letter of the respective surnames of the authors- Charlson, Lovelock, Andreae and Warren). They proposed that methane sulphonate (MSA) and non-sea-salt sulphate (NSS-SO_4^{2-}), common in marine environments, may be derived from the atmospheric breakdown of DMS. Hence it is a potential contributor to cloud condensation nuclei (CCN) since sulphur-dioxide resulting from burning of fossil fuels is an important contributor to CCN but limited to areas of high population density, whereas DMS would be dominant in large oceanographical provinces.

The sea salt particles are not typically found at cloud height and other particles such as nitrates (found on coarser particles) are not suitable for cloud condensation to occur due to their particle size whereas the NSS-SO_4^{2-} and MSA are said to be of a suitable particle size for cloud condensation, thus these particles are classed as CCN. Cloud formation takes place when water droplets condense onto particles

(CCN) acting as nuclei (Fig. 2). Cloud formation increases the cloud albedo. Increased cloud albedo results in more solar radiation being reflected back to space, leading to an overall climate cooling effect. Applying a Gaian approach, the authors proposed that increased cloud albedo has a coupling effect since increased DMS production by phytoplankton in warmer climates would induce climatic cooling by reducing temperature gain from solar radiation and this in turn induces lower DMS production during cold periods (Charlson et al. 1987).

The atmospheric concentration of DMS is several orders of magnitude below the value in equilibrium with seawater predicted by Henry's law (Andreae, 1990). The high DMS concentrations in the surface oceans, relative to its atmospheric levels, drive a significant sea-to-air flux of DMS. DMS is oxidised to sulphate in the atmosphere, combining with water drops to form acidic aerosols. The atmospheric lifetime of DMS is suggested to be 8-48 h (Chatfield and Crutzen, 1984; Luria et al. 1986), due to its oxidation by OH and NO₃ radicals.

2.2 International Scenario

Dimethyl Sulphide

DMS was reported first in oceanic waters by Lovelock et al. (1972). DMS concentrations vary substantially (Fig. 3) on a regional and seasonal basis (Kettle et al. 1999). In general, higher DMS levels are found in coastal areas and upwelling regions and Andreae (1990) has

reported concentration values of 2.8 and 4.9 nM for these areas, respectively. The most important paper to date concerning the overall global distribution of DMS is probably that of Kettle et al. (1999). Thirty two authors were involved in this study which created a huge global database of 15,617 point measurements gathered from a wide range of published and unpublished material reporting DMS concentration in surface waters. The database does not give a definitive global picture of DMS, because the measurements do not comprehensively cover the globe, but it does show general trends. The database has revealed that there is not much variation in the low latitudes, with an approximate average DMS concentration of 2.5 nM for the low and mid latitudes whilst in higher latitudes, the concentrations appear to be influenced by seasonal factors.

In north east Atlantic Ocean, DMS concentrations range from 0.1 to 19.3 nM (Groene, 1995). Belviso et al. (2000) reported low concentrations of <0.3 nM of DMS at South of Iceland. Matrai and Vernet, (1997) observed DMS concentrations of 2.8 – 25.3 nM, in the central Barents Sea. It was highly variable in North Sea, ranging from below 0.1 nM to 'hot spots' reaching 312 nM. The measurements indicate background concentrations of 2 to 4 nM off the western Iberia shelf (Uher et al. 2000). Along a transect extending from a Swedish fjord into the Gotland basin, the concentration varied from 0.5 to 2 nM (Leck et al. 1990). In the northwestern Mediterranean, the

concentrations ranged from 0.7 - 3.7 nM and values up to 19 nM off the Ebro and Rhone deltas and off Barcelona have been reported (Simó et al. 1995; Simó et al. 1997). In the Yellow sea the average DMS concentration in subsurface layer was reported to be 2.3 nM by Yang et al. (2006) and 2.89nM by Hu et al. (2005). Along the South Korean coast the reported concentration is 6.3nM (Lee et al. 2004) while in the east China Sea, it averaged about 3.4 nM (Yang et al. 2000). Niki et al. (2000) observed elevated DMS levels in Tokyo bay rising to 130nM. In Funka bay, Pacific coast of Japan, the concentration averaged to 6.6nM (Yang et al. 2005b).

DMS constitutes the 'odour of the sea' in coastal areas. Studies have indicated elevated DMS levels in estuaries (Simo et al. 1997; Iversion et al. 1989). The concentration of DMS varied for different ecosystems [e.g.Venice lagoon (16.3 nM), Moret et al. (2000), Danube estuary (11.9 nM), Amoroux et al. (2002), and Rhine estuary (10 nM), Sciare et al. (2002)]. Average concentrations in the Elbe, Ems, Scheldt, and Gironde estuaries fell within the range of 0.2 nM to 0.7 nM, and only the Loire (1.3 nM) and Rhine (4.2 nM) estuaries showed slightly higher levels (Sciare et al. 2002). In the Oosterscheldt, a former estuarine channel of the River Scheldt, the average DMS level in May 1985 was 7.0 nM and reached a maximum of 22.7 nM (Kettle et al. 1999). In the Canal de Mira, an elongated shallow arm extending south from the inlet of Ría de Aveiro (Portugal), its level varied from 2.9 to 5.3 nM

(Cerqueira and Pio, 1999). DMS concentrations in Toulon Bay in the north west Mediterranean Sea varied from 3.6 to 21 nM (average - 9.8 nM) (Despiau et al. 2002). The shallow lagoon of Venice in the northern Adriatic also displayed enhanced DMS levels around an annual average of 4.6 nM (Moret et al. 2000). Along the Pearl River estuary, it ranged from 0.05 to 52 nM (Hu et al. 2006). The Peru upwelling has a fairly constant average DMS concentration of 4 - 5 nM. During some measurements, the estuarine and river waters had lower DMS concentration than seawater and DMS concentration is often positively correlated with salinity. This finding has been attributed to algal speciation, because diatoms are often dominant in estuaries and generally are poor DMSP producers (Iverson et al. 1989; Sciare et al. 2002). The tropical regions have relatively high DMS concentrations year-round, whereas in temperate regions, especially the temperate coastal areas, a pronounced seasonality is evident with quite low values during the cold season.

Factors Affecting DMS Concentration

DMS release is affected by a variety of factors related to plankton population dynamics and trophic interactions. These include enhanced DMS release during cell lysis (Nguyen et al. 1988), zooplankton grazing (Dacey and Wakeham, 1986) and viral infection (Malin et al. 1998). In addition, competing DMSP degradation pathways also may be involved in DMS release (Kiene, 1992; Kiene, 1996). The

complexity of food web dynamics and geophysical interactions involved in DMS cycling make it difficult to explain geographical DMS distribution patterns. In temperate waters, DMS displays pronounced seasonal variability, characterized by summer maxima that coincide with low algal and DMSP abundance. Matrai and Vernet (1997) noted high DMS concentrations (2.8 – 25.3 nM), during a spring bloom in the central Barents Sea, dominated by diatoms and *Phaeocystis pouchetii*. The highest concentrations (up to 45 nM) were reported for south of Iceland during a summer coccolithophore bloom, (Holligan et al. 1993). Studies found a local maximum from 7 to 19 nM in areas of wind-driven upwelling off western Iberia (Uher et al. 2000). DMS 'hot spots' were also associated with frontal systems along western Ireland and the Celtic Sea shelf break (Turner et al. 1988; Locarnini et al. 1998; Baker et al. 2000; Uher et al. 2000), tidal fronts in the western English Channel and along the eastern UK coast (Holligan et al. 1987; Turner et al. 1988; Uher et al. 2000) and algal blooms in the northeastern North Sea (Turner et al. 1989). The seasonal variation of DMS was studied at a coastal station in the western Gotland basin. Results from this time series indicate concentrations below 0.3 nM before and after ice cover in December and March, enhanced concentrations following spring blooms in April/May, and a seasonal maximum of 15 nM around July/August. A seasonal maximum of 15 nM was observed along western Gotland basin was attributed to zooplankton grazing pressure

inferred from zooplankton abundance (Leck et al. 1990). DMS concentrations collected along a transect extending from a Swedish fjord into the Gotland basin showed the highest concentration near a sewage outlet within the fjord (Leck et al. 1990). DMS 'hot spots' with concentrations above 30 nM occurred mostly from May to July and was particularly abundant in the shallow waters of the southern North Sea along the Belgian, Dutch and German coasts (Liss et al. 1993; Turner et al. 1996), which were subjected to high nutrient loads and pronounced tidal mixing (Otto et al. 1990).

Open ocean surface seawater DMS concentrations generally range from 0.5 to 5 nM, and are the lowest during the winter months and highest during the summer months at high latitudes (Bates et al. 1987b). Large differences in DMS concentrations have been found in seasonal cycles in regions, like the Pacific Ocean (Bates et al. 1987b), the North sea (Turner et al. 1988), the Baltic sea (Leck et al. 1990), the northwest Atlantic ocean (Berresheim et al. 1991) and the coast of Japan (Uchida, 1993). Seasonal effects are arguably the most important control of DMS variability around the British islands. In North Sea concentrations < 0.1 nM were observed mostly in the winter months of January and February, and only occasionally during late autumn (October to December) and early spring (March to April). Turner et al. (1988) reported an approximately 70-fold difference between average DMS concentrations from January and July/August,

similar to seasonal amplitudes reported for the southern North Sea (Turner and Liss, 1985; Turner et al. 1989; Liss et al. 1993; Nedwell et al. 1994). In the northwest Mediterranean sea, DMS showed mean concentrations of 0.7 nM in April and 3.7 nM in June (Simó et al. 1997). In the Canal de Mira, average DMS levels were 2.9 nM and 5.3 nM in winter and summer, respectively, and reached levels up to 20 nM during summer maxima (Cerqueira and Pio, 1999). Interestingly, no clear, seasonal pattern was evident in Toulon Bay. Instead, it remained high throughout the year and showed peak concentrations of 15 nM in January. The elevated DMS levels in Toulon Bay were attributed to effects of anthropogenic inputs, which were particularly strong in the eutrophic, inner bay (Despiau et al. 2002). Available evidence suggests that these seasonal patterns are related to DMS cycling rates (Dacey et al. 1998; Uher et al. 2000), driven by biogeochemical and geophysical forcing that were recently parameterized by combinations of mixed layer depth, phytoplankton abundance, irradiance and nutrient limitation (Anderson et al. 2001; Simó and Dachs, 2002). Also physical factors such as temperature, vertical mixing, and flux to the atmosphere are also critical for the ultimate distribution and concentration of dissolved DMS in the water column (Dacey et al. 1998; Simó and Pedros-Alio, 1999, Yang et al. 2000).

Dimethyl Sulphide Flux

Bates et al. (1987a) gave a value of $0.5 \text{ Tmol year}^{-1}$ for oceanic DMS flux to the atmosphere while Andreae (1990) predicted $1.2 \text{ Tmol year}^{-1}$. Recently, based on mathematical model using huge global database (Kettle et al. 1999) derived oceanic DMS flux in the range of about $0.5 - 1 \text{ Tmol year}^{-1}$. However, Simo (2001) summarised global sulphur emissions into the atmosphere and derived an average oceanic DMS emission of $0.7 \text{ Tmol year}^{-1}$. Uher et al. (2000) observed a mean flux of $10.5 \mu\text{M m}^{-2} \text{ d}^{-1}$ in north east Atlantic Ocean whereas in north and south Atlantic, it was $6.0 \mu\text{M m}^{-2} \text{ d}^{-1}$ (Kettle et al. 2001). A flux of $8.1 \mu\text{M m}^{-2} \text{ d}^{-1}$ was measured along North Sea by Archer et al. (2002b). The flux data collected along north west Mediterranean had a value of $11.2 \mu\text{M m}^{-2} \text{ d}^{-1}$ in the shelf and $2.5 \mu\text{M m}^{-2} \text{ d}^{-1}$ in the open sea (Simo et al. 1995). Andreae (1986) had estimated flux of global coastal and shelf zones as $7.7 \mu\text{M m}^{-2} \text{ d}^{-1}$. An average of $14.8 \mu\text{M m}^{-2} \text{ d}^{-1}$ was estimated along the Irish Sea and English Channel by Turner et al. (1988). The flux of DMS along the intertidal regions in Norsminde Fjord, Denmark was $37.1 \mu\text{M m}^{-2} \text{ d}^{-1}$ (Jorgensen and Okholm - Hansen, 1985). Cerqueira and Pio (1999) reported a value of $0.7 \mu\text{M m}^{-2} \text{ d}^{-1}$ from the inlet of Ría de Aveiro (Portugal) whereas it was $0.3 \mu\text{M m}^{-2} \text{ d}^{-1}$ in Venice Lagoon (Moret et al. 2000). The large areas of low and moderate biological productivity contribute large amounts of DMS to the atmosphere comparable to those from the relatively small regions

of high productivity in the upwelling regions and the coastal areas. This is in contrast to earlier views (Graedel, 1979), which had assumed that the biogenic sulphur flux from the oceans would be dominated by localized 'hot spots' of biological productivity. Ocean margins have been identified as a significant source of DMS (Andreae, 1986; Leck and Rhode, 1991; Turner et al. 1996) and several results suggest that estuaries (Iverson et al. 1989) and corresponding plumes in the open sea (Turner et al. 1996; Simo et al. 1997) also could represent an important source of atmospheric DMS. However, up to now the only detailed studies on the importance of estuaries as a source of DMS originate from the work of Iverson et al. (1989) conducted in several Northern American estuaries and Cerqueira and Pio (1999) in a Portuguese canal.

Dimethylsulfoniopropionate

Oceanic phytoplankton plays an important role in the biogeochemical cycle of sulfur, providing a link between the oceanic and atmospheric cycle. DMSP, a tertiary sulfonium derivative of methionine, is found in many species of green and red macroalgae in habitats ranging from polar (Karsten et al. 1991) to temperate (White, 1982, Reed, 1983) to tropical (Bischoff et al. 1994, Dacey et al. 1994). The ecological role of DMSP may involve osmoregulation (Vairavamurthy et al. 1985; Dickson and Kirst, 1987), cryoprotection (Kirst et al. 1991), chemical

defence via acrylic acid formation (Wolfe et al. 1997) and antioxidant function (Sunda et al. 2002). DMSP is a tertiary compound that is thought to be generated from methionine (Challenger, 1951). The occurrence of DMSP in marine phytoplankton was first documented by Ackman et al. (1966). Haas in 1935 identified DMS emissions from the marine algae *Polysiphonia fastigiata* for the first time. The precursor of DMS, dimethyl sulfoniopropionate (DMSP), was isolated from this species by Challenger and Simpson (1948). It has been stated that DMSP is produced chiefly by certain classes of marine phytoplankton (Table.1) including Dinophyceae (dinoflagellates) and Prymnesiophyceae (including the coccolithophorids) (Keller et al. 1989). DMSP is produced in pure cultures of the phytoplankton species *Hymenomonas carterae* (Vairavamurthy et al. 1985) and *Gymnodinium nelsonii* (Dacey and Wakeham, 1986). High levels of DMSP were found in corals due to the presence of zooxanthellae (symbiotic dinoflagellates) (Broadbent and Jones, 2004).

Recent studies have shown that diatoms also contribute to the water column budgets of DMSP and DMS as much as *prymnesiophytes* (Matrai and Vernet, 1997). Some diatoms of the *Chrysophyceae* and *Bacillariophyceae* can also produce significant amounts of DMSP. Keller et al. (1989) studied 123 different types of phytoplankton species and their DMSP content and concluded that high intracellular DMSP concentrations were found in species that are members of the classes

Chrysophyceae, *Dinophyceae*, and *Prymnesiophyceae*. These species include *Chrysamoeba* sp., *Amphidinium carterae*, *Prorocentrum* sp., *Emiliana huxleyi* and *Phaeocystis* sp.

Table.1 Intracellular concentration of DMSP in marine phytoplankton

| Organism DMSP ^a (mM) | Cytosolic | Reference |
|-----------------------------------------------------------|-----------|--------------------------------|
| <i>Hymenomonas carterae</i> | 120 | Vairavamurthey et al. (1985) |
| <i>Gymnodinium nelsoni</i> | 280 | Dacey and Wakeham, (1986) |
| <i>Platymonas subcordiformis</i> | 170 | Dickson and Kirst, (1986) |
| <i>Phaeocystis</i> sp. | 71–169 | Stefels and van Boekel, (1993) |
| <i>Melosira numuloides</i> (Diatoms) | 264 | Keller et al. (1989) |
| <i>Chrysamoeba</i> sp. (chrysophyte) | 596 | |
| <i>Ochromonas</i> sp. (chrysophyte) | 529 | |
| <i>Prorocentrum</i> sp. Strain IIB2b1 (dinoflagellate) | 1,082 | |
| <i>Emiliana huxleyi</i> BT6 (coccolithophore) | 166 | |
| Diatoms (from sea water) | 38 | Turner et al. (1988) |
| <10- μ m flagellates | 125 | Belviso et al. (1990) |
| Dinoflagellates | 640 | |

^a Per liter of cell volume.

Other marine sources of DMSP

| Source DMSP | Concentration (mM) | Reference(s) |
|------------------------------|--------------------|-----------------------|
| <i>Spartina alterniflora</i> | 20–70 | Dacey et al. (1987) |
| Copepod fecal pellets | 0.17 | Tang (2001) |
| Microbial mat | 0.85 | Jonkers et al. (1998) |

Distribution

In order to understand DMS distribution better, an understanding of the distribution and cycling of the precursor, DMSP is essential. It was during the 1980's that some of the first field measurements of DMSP were taken up and subsequently published by Andreae (1990) and Turner et al. (1988). Published data of both dissolved DMSP (dDMSP) and particulate DMSP (pDMSP) measurements in seawater are not as

widely available as that of DMS measurements (Kettle et al. 1999). DMS measurement began earlier, perhaps due to the fact that the analysis was easier than that of DMSP.

The average DMSP concentration found in the global oceans is about 14 nM (Kettle and Andreae, 2000). For Antarctic waters, Turner et al. (1995) found DMSP concentrations of 12 nM for dDMSP and 26 nM for pDMSP. Data collected in north Atlantic showed a concentration of 27.3 nM (Yang et al. 2005a) whereas in north east Atlantic it was 133.5 nM during summer bloom (Malin et al. 1993). Andreae (1990) found dDMSP in the range of 4 - 6 nM and pDMSP in range of 10 - 14 nM for north west Atlantic. Matrai et al. (2007) gave values ranging from 10 – 93.0 nM in Barents Sea. Simo et al. (1997) have observed 3nM concentration in the Mediterranean Sea. Kiene and Linn (2000b) found low dDMSP and pDMSP values of 1.5 nM and 7 nM (oligotrophic oceanic waters) and 3 nM and 15 nM (shelf waters), respectively in the Gulf of Mexico. High DMSP concentrations (3 – 4 μ M) were observed in Barcelona Harbor (Belviso et al. 2000). DMSP levels ranging from 5.2nM - 11.3nM DMSP were reported in a Portugal canal, Ría de Aveiro (Cerqueira and Pio, 1999). Sciare et al. (2002) observed a mean value of 2.6nM of DMSP in 6 European estuaries (Scheldte, Gironde, Rhine, Ems, Elbe, Loire estuaries). DMSP values ranged from 2.1 - 58.8 nM in Little Bay of Toulon (Jean et al. 2005). In Funka bay it averaged to 7.9 nM for dissolved fraction whereas for particulate

fraction it was 33.2 nM (Yang et al. 2005b). Iversion et al.(1989) observed DMSP levels in the range of 0.3 – 28 nM for the dDMSP whilst for the particulate fraction the concentration ranged from 2.9 – 150 nM in north American estuaries (Delaware Bay, Chesapeake and Ochlockonee Bay).

Factors Affecting DMSP Concentration

The most fundamental control of DMS (P) is the phytoplankton species composition. Only a limited number of species produce high concentrations of DMSP, mainly belonging to the classes *Haptophyceae* and *Dinophyceae* (dinoflagellates), some diatoms (*Bacillariophyceae*) may also produce significant amounts of DMSP (Keller et al. 1989). It should be noted that, although some species do not produce large concentrations of DMSP, because they occur in large blooms, the concentration of DMSP in the water column is correspondingly high. Keller et al. (1989) stated that the high DMSP (and resulting DMS) concentration in seawater is largely influenced by the size and duration of blooms of DMSP producing phytoplankton. Examples of these blooms include *Phaeocystis pouchetii* in the coastal Antarctic (Gibson et al. 1990), *Phaeocystis* sp. off the Dutch coast (Stefels et al. 1996), *Emiliania huxleyi* in the northeast Atlantic (Holligan et al. 1993), northern North Sea (Hatton, 2002) and in the Gulf of Maine (Matrai and Keller, 1993). DMSP is also found during

blooms of *Ceratium lineatum*, *Cyclococcus leptoporus*, and *Gyrodinium aureolum* (Turner et al. 1988). Within phytoplankton blooms, Malin et al. (1993) found DMSP concentrations of ~37 nM (dDMSP) and ~97 (pDMSP) for a coccolithophore bloom in north east Atlantic and Turner et al. (1988) found similar values of ~39 nM for dDMSP and ~90 for pDMSP within phytoplankton blooms in coastal waters of UK. Archer et al. (2002b) recorded lower DMSP concentrations (particularly for dDMSP) for an evolving coccolithophore bloom (dDMSP - 5.6 nM, pDMSP - 49 nM). Similarly, Scarratt et al. (2000b) observed lower DMSP concentrations for an evolving *Chromulina* sp. bloom (dDMSP-12 nM, pDMSP-79 nM). In marine sediments, DMSP might originate from *Spartina* leaves (Dacey et al. 1987) or macroalgae, like *Ulva lactuca* (Dickson et al. 1982) and *Enteromorpha intestinalis* (Edwards et al. 1987). Hence, the seawater concentrations of DMSP may be controlled by the total algal biomass and the composition of the plankton community. In addition, external factors such as salinity, temperature, and nutrient availability may also affect the level of DMSP in seawater (Turner et al. 1988; Bucciarelli and Sunda, 2003). The physiological condition of the phytoplankton cells, mediated by abiotic parameters (light, nutrients, temperature and salinity) is also important. The production of DMSP by phytoplankton is increased under high light and high salinity conditions. In Sargasso Sea, an oligotrophic region, the maximum (summertime) concentration recorded was 20 nM

for dDMSP and 27 nM for pDMSP (Dacey et al. 1998), whereas Ledyard and Dacey (1996) found a dDMSP range of 2 – 9 nM during winter and spring for this region. A winter value of 5.2 nM and summer value of 11.3 nM DMSP were reported by Cerqueira and Pio, (1999) in Ría de Aveiro (Portugal). According to Liss et al. (1993) temporal profile of DMSP concentrations is defined by a strong seasonality in temperate waters particularly in coastal area. Additionally, a less conclusive relationship has been proposed between DMSP production and nutrient limitation. Matrai et al. (2007) observed DMSP concentrations to be a function of seasonality, water masses, grazing and nutrient limitation.

Studies that have quantified the size of source and sinks of DMS and DMSP in the upper ocean sulfur cycle have proved invaluable in understanding the factors that control the concentration of DMS (P) in surface waters (Archer et al. 2002a). The flux of DMS from the surface ocean to the atmosphere is in fact a very minor sink. Bacterial consumption of DMS seems to be the largest sink, and enzymatic cleavage of DMSP to DMS is an important source. On the whole, DMSP synthesis by marine photoautotrophs accounts for about 50×10^{12} moles of sulfur per year. As each molecule of DMSP contains five atoms of carbon, its synthesis is important in the carbon cycle; its production is estimated to account for 3–10% of the global marine primary production of carbon (Kiene et al. 2000), and its degradation

supplies about 3–10% of the carbon requirements of heterotrophic bacteria in surface waters (Simó et al. 2002). Dimethylsulfoniopropionate is a significant component of the organic matter that flows through the microbial food web. During blooms of DMSP producing phytoplankton, it can represent ≥ 50 % of sulphur and ≈ 10 % of carbon fluxes through various trophic levels namely phytoplankton, bacteria and microzooplankton. The importance of DMSP in biogeochemical cycling is magnified by its role as the main precursor of volatile DMS. DMS is formed from DMSP by enzymatic cleavage via algal or bacterial DMSP lyase (Stefels and van Boekel, 1993; Ledyard and Dacey, 1994) along with acrylic acid. DMSP lyase activity (both intracellular and extracellular) also has been found in marine bacteria (Yoch et al. 1997). Currently available inhibition methods do not allow one to distinguish between DMSP lyase in bacteria or phytoplankton or even microzooplankton (Steinke et al. 2002; Yoch, 2002). The study of DMSP transformations can serve as model to better understand the microbial cycling of labile DOM and possible linkages between marine microbiota and atmospheric composition. It is rapidly cycled by microorganisms in the upper ocean with turnover times that typically range from 0.1 to 1 day. In temperate waters, DMSP utilization is a widespread feature among different groups of bacterioplankton (Vila et al. 2004; Malmstrom et al. 2004a). It is reported that DMS utilization as a growth substrate was carried out

by specialists (Vila et al. 2006). This specialization in microbial DMS metabolism contrasts with that of dissolved DMSP, the biochemical precursor of DMS, which is consumed by a wide spectrum of marine bacteria (Malmstrom et al. 2004b; Vila et al. 2004). This difference is reflected in the turnover times of both compounds in the surface ocean. While dissolved DMSP turns over typically in 0.1–1 day (Kiene and Linn, 2000a; Zubkov et al. 2002; Malmstrom et al. 2005), DMS generally turns over in 0.5– 4 days (Simó, 2004). The conversion of algal DMSP into volatile DMS is not direct but tightly coupled with a number of biochemical and trophic processes (Fig. 4) in the water column (Simo et al. 2002), such as enzymatic activities (Stefel et al. 1995; Steinke et al. 1998), bacterial activities (Kiene, 1992; Ledyard and Dacey, 1996), herbivorous and carnivorous grazing (Dacey and Wakeham, 1986; Belviso et al. 1990; Kwint et al. 1996; Archer et al. 2001a).

Bacteria from diverse lineages can convert dissolved DMSP into DMS (Yoch, 2002) and free-living, DMSP-cleaving bacteria are ubiquitous in the marine environment (Diaz et al. 1992; Visscher et al. 1992; Ledyard and Dacey, 1994). Bacteria that grow solely on DMSP as organic carbon source have also been isolated from various oceanic settings (Diaz et al. 1992; Visscher et al, 1992; Ledyard et al. 1993; Ledyard and Dacey, 1994; Visscher and Taylor, 1994). Bacterial assemblages present in DMSP producing blooms in surface waters

include *Rosebacter*, SAR86 and SAR11 lineages in North Atlantic (Gonzalez et al. 2000) and *Rosebacter*, SAR86 and *Cytophaga-Flavobacterium* lineages in the North Sea (Zubkov et al. 2002). Experiments carried out on some strains of heterotrophic marine bacteria by Wolfe and Steinke (1996) revealed that, when placed under conditions that cause osmotic stress, some strains of heterotrophic marine bacteria undergo active uptake of DMSP, suggesting a potential osmotic function. Work involving tracer studies of ³⁵S-DMSP on various seawater samples, showed that most DMSP is consumed by bacteria (Fig. 5.) in less than 3 hours and that a mean of 33% ended up as particulates (cellular protein), 46% as dissolved non-volatile degradation products (i.e. sulphates and DOM-metal complexes) and 9% as volatile products (mostly MeSH and DMS to a lesser extent) Kiene and Linn, 2000b). Daily bacterial consumption rates of DMSP in the Gulf of Mexico were established by (Kiene and Linn, 2000a). The rate was 3.8 nM d⁻¹ (turnover time: 8.2 hours) in oligotrophic shelf waters and 39 nM d⁻¹ (turnover time: 1.8 hours) in mesotrophic shelf waters. In the North Sea, Zubkov et al. (2002) obtained similar mean consumption rates of 20 nM d⁻¹ (turnover time- 10 hours) for the surface water layer (top 13 – 30 m) and 41 nM d⁻¹ (turnover time- 2 hours) for the subsurface layer. Mass balance calculations suggest that algal-derived DMSP and DMS are rapidly recycled in the upper ocean and that only approximately 1% of DMSP

is lost to the atmosphere as DMS (Andreae, 1990; Archer et al. 2002a).

Bacterioplankton are the main agents in the turnover of dissolved DMSP through two main pathways (Fig. 6). DMSP can be directly cleaved to DMS mediated by enzyme DMSP lyase or DMSP may undergo demethylation (Taylor and Gilchrist, 1991; Visscher and Taylor, 1994). The latter route can be followed by a second methylation, resulting in non-volatile sulfur compounds (Visscher et al. 1992), or by a demethiolation that leads to metanethiol (MeSH) formation, which goes primarily into bacterial macromolecules (Kiene et al. 1999a; Kiene and Linn, 2000b).

Growing evidence shows that non-DMS producing pathways are perhaps more common than DMSP cleavage in the marine environment (Kiene and Service, 1991; Kiene, 1992; Visscher et al. 1992; Ledyard and Dacey, 1996). The breakdown of DMSP to DMS and acrylic acid accounted for less than 30% loss of the total DMSP. Kiene and Linn (2000a) found a mean of 10% of DMSP was converted to DMS in seawater samples from the Gulf of Mexico. Kiene and Linn, (2000a) and Scarratt et al. (2000a) found the quantities of DMS produced from DMSP were partly influenced by the availability of DMSP to bacterial demethylation, which results in increased DMS production when higher levels of DMSP are present. In addition to funneling most of the DMSP away from DMS production, bacteria

control the emissions of DMS by consuming a large fraction of the DMS produced and converting it into the nonvolatile products dimethyl sulfoxide (DMSO) and sulfate (del Valle et al. 2007).

Recently Vila et al. (2007) reported that members of Alpha-Proteobacteria and Gamma Proteobacteria accounted for most of the DMSP assimilating cells over the year in surface sea waters from Blanes Bay. Bacteria not only cleave some of the DMSP to DMS, but also act as the major sink for DMS in surface waters. Bacterial strain MWYL1; belonging to genus *Marinomonas* from root surfaces of the salt marsh grass *Spartina anglica* grew with DMSP as the sole carbon source (Todd et al. 2007). Only 1.3 % of the DMSP synthesized by the photosynthetic eukaryotes entered the atmosphere. Minor changes in the metabolism of any of the microbial groups could have a major impact on the level of DMS sea-to-air flux (Archer et al. 2004).

Microbial cycling of volatile organic sulfur compounds (VOSCs), especially dimethyl sulfide (DMS) has to be studied because of its important role in the processes of global warming, acid precipitation, and the global sulfur cycle. The lifetime of DMS in surface waters is of the order of one day (Kiene and Bates, 1990) as it is degraded both microbially (Taylor and Kiene, 1989) and photochemically (Brimblecombe and Shooter, 1986) and lost to the atmosphere via air-sea exchange (Fig 7). Biological DMS consumption in contrast was

found to be 3 - 430 times faster than DMS loss to the atmosphere in a tropical pacific water sample (Kiene and Bates, 1990). The biological DMS turnover time, that is the time needed for complete consumption of the DMS in the water, is 0.6 - 4.6 days. Consistent turnover times for biological consumption were found in Sargasso Sea waters, ranging from 0.5 - 2.1 days (Kiene, 1992). A recent experimental study showed that *Methylophaga* spp., a genus known to metabolize DMS, is a prominent group that developed in seawater enriched with DMS (Vila-Costa et al. 2006; Schafer, 2007). Dimethyl sulfide (DMS) released from the sea is an important compound in global sulfur circulation and global climate regulation. However, more than 10 times the amount of DMS released to the atmosphere is degraded in the sea by microorganisms. DMS is degraded or transformed by terrestrial and marine microorganisms via methyl mercaptan (MM) or dimethyl sulfoxide (DMSO). Some strains of sulfur oxidizers and methylotrophs degrade DMS via MM. Ammonia oxidizers, methanotrophs, algae, and some strains of phototrophs transform DMS to DMSO. Some terrestrial heterotrophic bacterial strains also have been found to degrade or transform DMS via DMSO. *Comamonas acidovorans* DMR-11 (originally *Pseudomonas acidovorans*) isolated from peat bio-filters transformed DMS to DMSO in the medium containing other organic carbon sources, such as sodium malate. A dibenzothiophene-desulfurizing bacterium, *Rhodococcus* sp. strain SY1, was able to

degrade DMS in the oxidative pathway via DMSO, and genes encoding an enzyme that oxidized DMS to DMSO have been cloned from *Acinetobacter* sp. strain 20B, which was able to grow on DMS as the sole sulfur source. Marine heterotrophic bacterium that belongs to the β subclass of the class *Proteobacteria* is able to utilize DMS as the sole sulfur source only in the presence of light. Schafer (2007) identified bacterial populations from a broad phylogenetic range in a mixed DMS-degrading enrichment and the dominant members were reported to be of the genera *Methylophaga* and *Alcanivorax*. They also included isolates belonging to *Gamma*- and *Beta* *Proteobacteria* and to the *Actinobacter* phylum.

Oceanic emissions of DMS are controlled by its concentration in surface seawater. Therefore, it is necessary to clarify the processes of production and consumption of DMS, but their detailed mechanisms have not been fully evaluated. There are several factors determining the concentration of DMS in surface water. Biological processes are largely responsible for the in situ production rate of DMS (Schultes et al. 2000; van Duyl et al. 1998). According to a recent investigation (Bates et al. 1994) DMSP and DMS constitute 24% and 1% respectively of the total organic sulfur in filterable material in a marine environment. DMS production from cleavage of DMSP accounted for 25% of the total biogenic sulfate assimilation, but only 1 - 2% of the DMS was released to the atmosphere. A similar estimate for the

fraction of reduced sulfur which is ventilated as DMS to the atmosphere was given by Andreae (1985). The DMS flux to the atmosphere therefore possibly represents only a minor loss mechanism for the total amount of DMS produced in the sea. As by far larger part may be consumed and recycled inside the water column by biotic processes. Knowledge of the biogenic processes which produce and consume DMS is needed to understand the variation in DMS fluxes to the atmosphere as well as to quantify the potential for DMS production marine systems in present, past and future.

2.3 National Scenario

Studies regarding the spatial distribution of the volatile gas, DMS and its precursor – DMSP in waters surrounding the Indian peninsula were initiated by National Institute of Oceanography, Goa. Since then levels of DMS and DMSP have been measured in various regions but a thorough study is still eluding us. DMS concentrations studied In the Indian Ocean revealed significant interannual variations from 1998 to 1999. Mean DMS concentration was five times higher in 1999 (3.32 nM and DMSP 16.36) than compared to 1998 observations (DMS - 0.7 nM and DMSP - 3.31nM). In 2001, measurements were made for DMS and DMSP in the Bay of Bengal. An average DMS concentration of 1.8 ± 1.9 nM was observed, while DMSP concentrations varied between 0.7 nM and 40.2 nM with a mean of 10.4 ± 8.2 nM. The Arabian Sea

contained more DMS (mixed layer average was 7.8 nM) followed by the Bay of Bengal (2.8 nM) and the Central Indian Ocean (2.7 nM) (Shenoy, 2002). In Zuari estuary, at a site nearby Marmagoa Port trust, the DMS concentration varied from 0.3 and 15.4 nM while that of DMSP ranged from 0.8 to 419.5 nM (Shenoy and Patil, 2003). The highest concentrations of DMS and DMSP (525 and 916 nM, respectively) were found in upwelling regions along the west coast of India during the southwest monsoon and fall intermonsoon season (Shenoy and Kumar, 2007). An average value of $0.6 \mu\text{mol m}^{-2} \text{d}^{-1}$ flux has been reported from Zuari estuary by Shenoy and Patil (2003). The total diffusive flux of DMS from the Arabian Sea, Bay of Bengal and north Indian Ocean to atmosphere is estimated to be about $16 - 25 \times 10^{12} \text{ g S y}^{-1}$, which contributes to 4.1 - 6.3% of the global DMS emission (Shenoy and Kumar, 2007).

Though studies have been conducted spatially and sequentially in waters around Indian peninsula, it has been limited to the chemical aspects, mainly the concentration of DMS (P) and the distribution of phytopigments. Studies pertaining to bacterial role in DMS (P) dynamics have not been carried out so far. A few attempts have been made to comprehend the dynamics of these organic sulphur compounds both at macro and micro level in estuaries worldwide. The present study makes an endeavor to comprehend the role of bacteria

along with other physico - chemical and biological variables in the dynamics of DMS (P), at a less perturbed spot in Dona Paula Bay.

Twenty years after the appearance of the CLAW hypothesis, the biogeophysical – biogeochemical DMS system still draws such scientific interest that great research efforts are invested in the study of DMS and DMSP to the extent that these two tiny molecules are perhaps the organic substances for which distribution and cycling in the ocean are the best known (Simó, 2001). Owing to its transversal nature across disciplines, DMS(P) research is stimulating important advances in marine science fields as diverse as the physiology and elemental composition of microorganisms, chemosensory strategies, enzymology, sulfur fluxes in food webs, photochemistry and photobiology, and air–sea exchange. Each of these research fields has its own relevant scale in time and space. There is no doubt that any changes in albedo over oceanic areas could have important climatic effects. Improved knowledge of the marine sulphur cycle would allow for accurate quantification of sulphur fluxes to the atmosphere that drive the production of aerosols and possible subsequent changes to cloud cover. From a scientific point of view, the argument could be made that the ecological roles played by DMSP within the marine biological communities are equally, if not more interesting than the potential climate feedback interaction. The emerging knowledge in this field strengthens the arguments that DMSP is a molecule of central

importance to the biogeochemistry and ecology of marine communities. However, this will only be made possible by greater understanding of the processes which control DMS (P) production. This will only be achieved by further field and laboratory experiments to constraint the production rates of these sulphur species under differing physical, chemical and biological conditions.

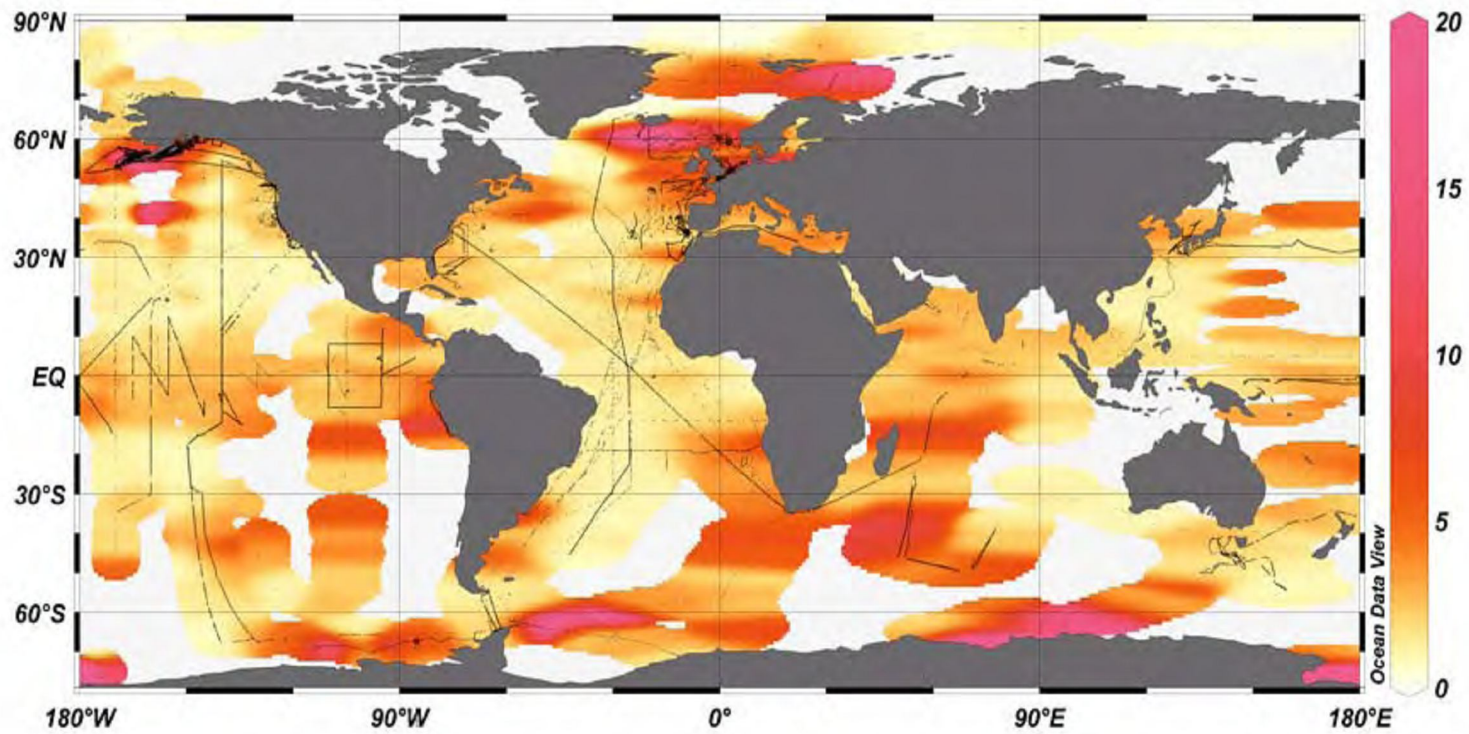


Fig. 4 Global surface DMS concentrations capped at 20 nM to aid readability; maximum concentrations measured exceed 300 nM. Source - global DMS database <http://saga.pmel.noaa.gov/dms/> (Kettle et al., 1999; Kettle and Andreae, 2000). Plot produced using *Ocean Data View* (<http://odv.awibremmerhaven.de/home.html>)

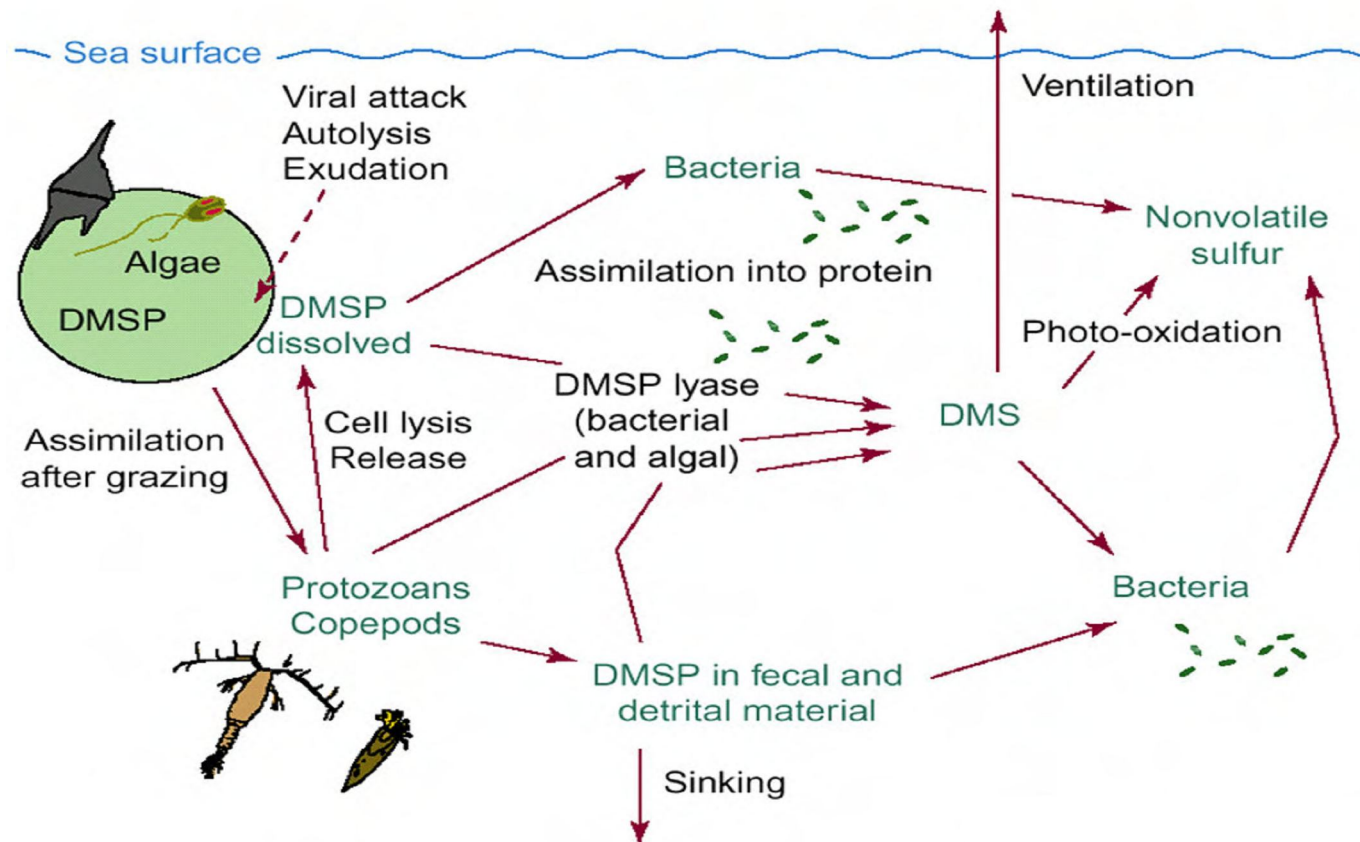


Fig. 5 The fate of phytoplanktonic DMSP in seawater (figure taken from Simo, 2001)

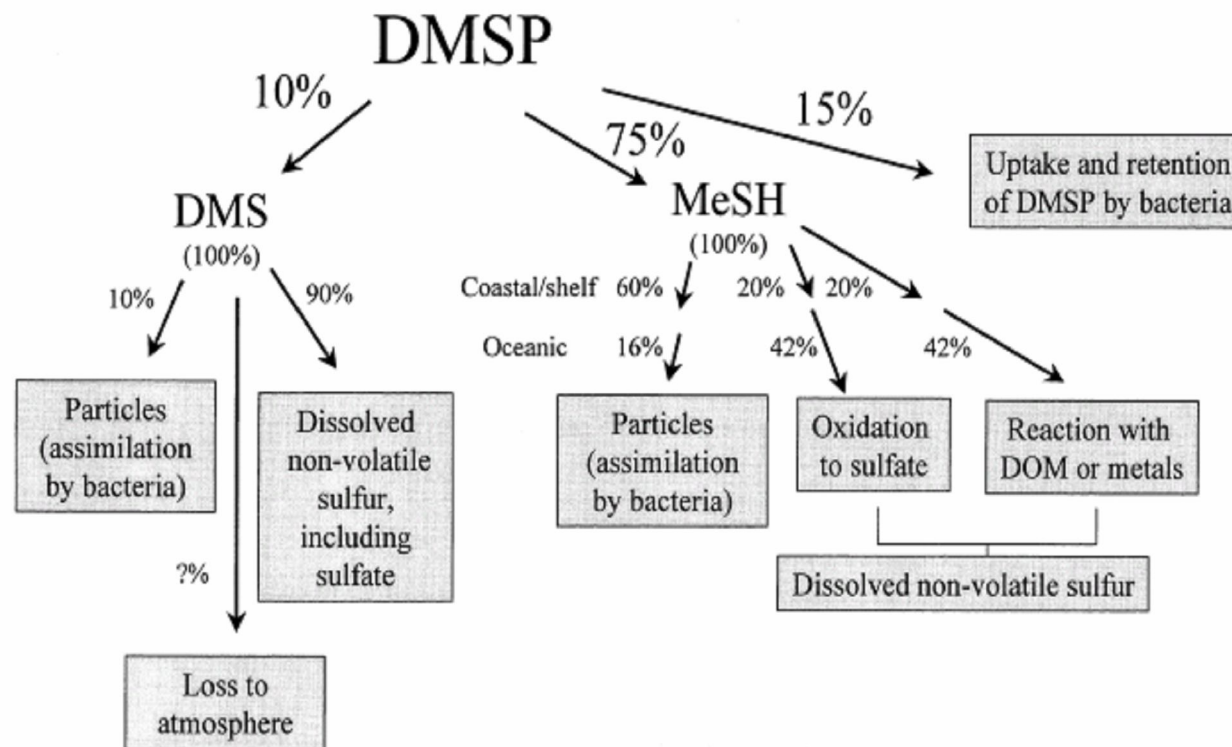


Fig.6 Generalized view of the paths and fate of sulphur from dissolved DMSP (figure taken from Kiene and Linn, 2000)

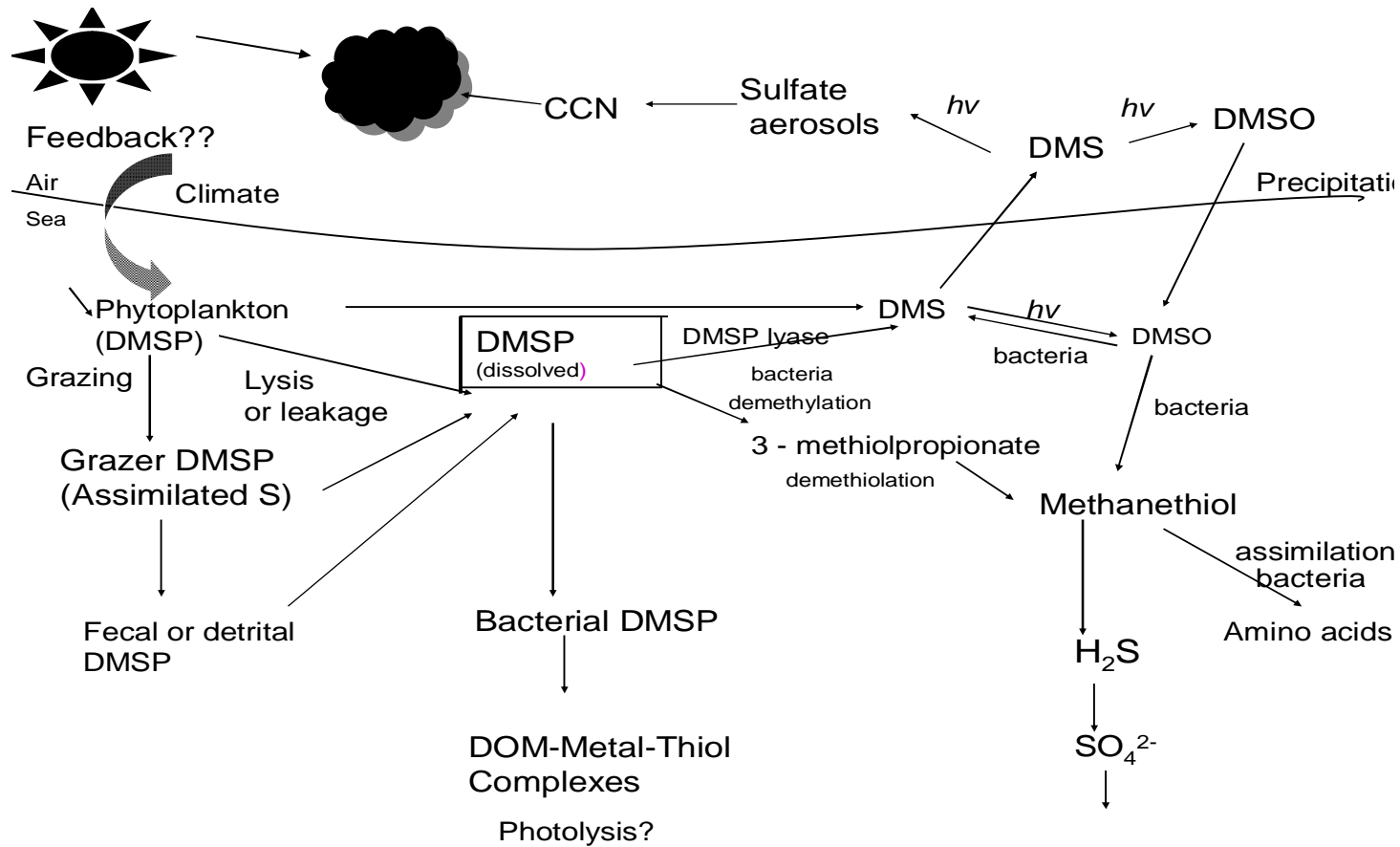


Fig. 7 Pathways of DMSP cycling in the ocean

