Microbial degradation of dimethylsulphide and related C₁-sulphur compounds: organisms and pathways controlling fluxes of sulphur in the biosphere

Hendrik Schäfer¹,*, Natalia Myronova¹ and Rich Boden²

¹ Warwick HRI, University of Warwick, Wellesbourne CV35 9EF, UK
² Biological Sciences, University of Warwick, Coventry CV4 7AL, UK

* To whom correspondence should be addressed: H.Schaefer@warwick.ac.uk

Received 23 July 2009; Revised 30 October 2009; Accepted 3 November 2009

Abstract

Dimethylsulphide (DMS) plays a major role in the global sulphur cycle. It has important implications for atmospheric chemistry, climate regulation, and sulphur transport from the marine to the atmospheric and terrestrial environments. In addition, DMS acts as an info-chemical for a wide range of organisms ranging from micro-organisms to mammals. Micro-organisms that cycle DMS are widely distributed in a range of environments, for instance, oxic and anoxic marine, freshwater and terrestrial habitats. Despite the importance of DMS that has been unearthed by many studies since the early 1970s, the understanding of the biochemistry, genetics, and ecology of DMS-degrading micro-organisms is still limited. This review examines current knowledge on the microbial cycling of DMS and points out areas for future research that should shed more light on the role of organisms degrading DMS and related compounds in the biosphere.

Key words: Metabolic pathways, methylotrophy, sulphur cycle.

DMS and related organic sulphur compounds

Volatile sulphur compounds play an important role within the biogeochemical cycle of sulphur. In being able to transfer from the liquid into the gas phase and vice versa, reduced volatile sulphur compounds have particular importance for affecting the composition and chemistry of the atmosphere. Although carbonyl sulphide (COS) has the highest concentration of the reduced volatile sulphur compounds in the atmosphere, dimethylsulphide (DMS) has the highest source strength (Watts, 2000) and is thought of as a climate-cooling gas (Charlson et al., 1987). DMS is produced by a variety of chemical and biological processes, both natural and man-made, and it is itself subject to a wide variety of chemical and biological transformations in the environment. Some aspects of the microbial metabolism of the related compounds (Table 1) dimethylsulphonpropionate (DMSP), dimethylsulphoxide (DMSO), dimethylsulphone (DMSO₂), methanethiol (MT), and methanesulphonic acid (MSA) are also considered where appropriate as these occur as precursors and/or degradation products of DMS.

Industrial roles of DMS and related compounds.

From an anthropocentric point of view, DMS and the related compounds DMSO and DMSO₂ are of particular interest in terms of their roles as flavour compounds and their industrial applications. DMS is a colourless liquid with a boiling point of 41°C and has a disagreeable odour akin to that of rotting cabbage. In our daily lives it is often present at low concentrations as an important flavour compound in a wide range of foods, including raw and processed fruits and vegetables such as tomatoes, sweetcorn, grapes, asparagus, and brassicas (Miers, 1966; Wong and Carson, 1966; Bills and Keenan, 1968; Kubec et al., 1998; Ulrich et al., 2001; Buttery et al., 2002; Segurel et al., 2004), cheeses (Milo and Reineccius, 1997; McGugan, 2002), honey (de la Fuente et al., 2007), and truffles (Talou et al., 1987). DMS is equally important as a flavour compound in a variety of beverages including beers (Meilgaard, 2002),
hydrogen sulphide (Lovelock much more abundant in the marine boundary layer than Lovelock and colleagues showed that dimethylsulphide was in marine air (Saltzman and Cooper, 1989), however, atmosphere that provided a precursor for sulphate aerosols sulphide was the volatile sulphur compound emitted into the oceans to the continents (Fig. 1). Prior to the work by Lovelock and colleagues it was assumed that hydrogen about the importance of DMS and other small molecular weight organic sulphur compounds in the environmental context alluded to in the introduction (see also Section 4.2). The roles of C1-sulphur compounds in an industrial and human context as described above are eclipsed by the major functions of these compounds in the environment, which have stimulated a substantial body of research over the last three decades. Chemical weathering of rock and the water solubility of sulphate lead to the loss of sulphur from the continents due to surface water runoff to the oceans. The oceans are rich in sulphur, having a sulphate concentration of approximately 28 mM. Emission of sulphur species from the marine environment into the atmosphere, their atmospheric transport, and subsequent deposition by wet and dry deposition on the continents are thus an important link in the sulphur cycle, affording sulphur transport from the oceans to the continents (Fig. 1). Prior to the work by Lovelock and colleagues it was assumed that hydrogen sulphide was the volatile sulphur compound emitted into the atmosphere that provided a precursor for sulphate aerosols in marine air (Saltzman and Cooper, 1989), however, Lovelock and colleagues showed that dimethylsulphide was much more abundant in the marine boundary layer than hydrogen sulphide (Lovelock et al., 1972). Based on these findings it was realized that DMS provides a route for sulphur transport between the oceans and the terrestrial environment (Nguyen et al., 1978). It is now well established that DMS is the most abundant form of biogenic sulphur input into the atmosphere; estimates range from 19–50 Tg of sulphur that are emitted as DMS from the marine environment per annum (Andreae, 1990). 20 Gg corre-

Environmental significance of DMS and related compounds

The roles of C1-sulphur compounds in an industrial and human context as described above are eclipsed by the major functions of these compounds in the environment, which have stimulated a substantial body of research over the last three decades. Chemical weathering of rock and the water solubility of sulphate lead to the loss of sulphur from the continents due to surface water runoff to the oceans. The oceans are rich in sulphur, having a sulphate concentration of approximately 28 mM. Emission of sulphur species from the marine environment into the atmosphere, their atmospheric transport, and subsequent deposition by wet and dry deposition on the continents are thus an important link in the sulphur cycle, affording sulphur transport from the oceans to the continents (Fig. 1). Prior to the work by Lovelock and colleagues it was assumed that hydrogen sulphide was the volatile sulphur compound emitted into the atmosphere that provided a precursor for sulphate aerosols in marine air (Saltzman and Cooper, 1989), however, Lovelock and colleagues showed that dimethylsulphide was much more abundant in the marine boundary layer than hydrogen sulphide (Lovelock et al., 1972). Based on these findings it was realized that DMS provides a route for sulphur transport between the oceans and the terrestrial environment (Nguyen et al., 1978). It is now well established that DMS is the most abundant form of biogenic sulphur input into the atmosphere; estimates range from 19–50 Tg of sulphur that are emitted as DMS from the marine environment per annum (Andreae, 1990). 20 Gg corre-

Atmospheric oxidation of DMS and the CLAW hypothesis

In the atmosphere, DMS is subject to chemical and photochemical oxidation resulting in a range of organic and inorganic sulphur species, mainly sulphate, sulphur dioxide, and methanesulphonic acid (MSA) (Panter and Penzhorn, 1980; Hatakeyama et al., 1982; Pham et al., 1995), but DMSO and DMSO2 are also formed (Harvey and Lang, 1986; Zhu et al., 2003), and DMSO has been detected in rain water (Ridgeway et al., 1992; Kiene and Gerard, 1994; Sciare et al., 1998). The atmospheric residence time of DMS is short, only about a day, and the main atmospheric sinks are believed to be the daytime oxidation with hydroxyl radicals and reaction with nitrate radicals during the night; however, it appears that the reactions removing DMS and their rate constants are complex and not yet well understood in detail (see Barnes et al., 2006, for a review). As indicated above, the atmospheric transport and subsequent dry and wet deposition of these sulphur compounds on the continents provide an important link in the global sulphur cycle. In soils, atmospherically derived sulphur contributes to the pool of sulphur available for assimilation as a plant nutrient, directly as sulphate, or indirectly after microbial regeneration of sulphate from organic sulphur compounds such as MSA, DMSO, and DMSO2 (see Kertesz, 2000, for

Table 1. DMS and related organic sulphur compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylsulphide (DMS)</td>
<td>(CH3)2-S</td>
</tr>
<tr>
<td>Dimethylsulphono-propionic acid (DMSP)</td>
<td>(CH3)2-S-C2H3-COOH</td>
</tr>
<tr>
<td>Dimethylsulphoxide (DMSO)</td>
<td>(CH3)2-SO</td>
</tr>
<tr>
<td>Dimethylsulphone (DMSO2)</td>
<td>(CH3)2-SO2</td>
</tr>
<tr>
<td>Methanethiol (MT)</td>
<td>CH3-SH</td>
</tr>
<tr>
<td>Dimethyldisulphide (DMDS)</td>
<td>CH3-S-S-CH3</td>
</tr>
<tr>
<td>Methanesulfonic acid (MSA)</td>
<td>CH3-SO3H</td>
</tr>
</tbody>
</table>

Fig. 1. Simplified scheme of the major pathways of DMS production and transformation in the marine environment. DMS emission into the atmosphere is a source of heat-reflecting aerosols that can serve as cloud condensation nuclei and thereby affect the radiative balance of the Earth, thus linking DMS production to climate regulation. Atmospheric transport of DMS and its oxidation products and deposition in the terrestrial environment provides an important link in the global sulphur cycle. The role of microbes as sinks for DMS is discussed in the text.

DMSO is a water-soluble polar organic solvent that is useful in a range of industries, and is also relevant as a pharmaceutical drug delivery agent that can facilitate the movement of various compounds across lipid membranes (Leake, 1967). Both DMSO and DMSO2 are found in a wide range of foods including milk (Pearson et al., 1981). Humans excrete 4–11 mg of DMSO2 per day via urine. Marketed as methylsulphonylmethane, it is also a constituent of some dietary supplements (see Parcell, 2002, for a review).
a review). The atmospheric oxidation products of DMS form aerosol particles which have direct and indirect effects that lead to negative temperature forcing of the Earth–atmosphere system, directly reflecting solar radiation and indirectly by providing particles that can act as cloud condensation nuclei (CCN) in the atmosphere. An increase in the number of CCN facilitates the formation of clouds that have a higher number of relatively smaller water droplets, thereby increasing the cloud albedo and decreasing the amount of solar radiation to reach the Earth’s surface. Hence, atmospheric DMS has been linked to climate regulation and is considered as a climate-cooling gas (Charlson et al., 1987). Charlson and colleagues hypothesized that production of DMSP by phytoplankton in the oceans was the basis of a geophysiological feedback loop that regulates global climate, also known as the CLAW hypothesis according to the first letters of the authors’ surnames (Charlson et al., 1987). The CLAW hypothesis states that an increase in solar irradiation and climate warming stimulates phytoplankton growth in the oceans and leads to an increased production of DMSP in the surface ocean, causing a greater flux of DMS into the atmosphere. The associated increase of DMS-derived aerosol particles in the atmosphere causes more solar radiation to be reflected, either directly by aerosols or indirectly through the intensified formation of high albedo clouds; ultimately these consequences of DMS emission are predicted to cause a cooling of the Earth’s climate. Climate cooling and a reduction of the amount of photosynthetically active radiation reaching the ocean surface, due to increased albedo, cause a decrease in phytoplankton growth and lead to a reduction of DMSP production in the ocean, a concomitant decrease in DMS emission and, therefore, an easing of the aforementioned negative temperature forcing; the phytoplankton DMSP/DMS system is therefore suggested to form a negative feedback loop (Charlson et al., 1987).

Vallina and Simó found that marine DMS concentrations are positively correlated with solar radiation dose (Vallina and Simó, 2007), which might lend support to the CLAW hypothesis as an increase of solar radiation would be expected to cause climate warming and increased DMS emission. Different approaches of modelling the expected increase of marine DMS production under global warming scenarios, however, have suggested only a modest 1–2% increase in DMS production, which is much weaker than the observable seasonal variations of DMS (Bopp et al., 2003; Vallina et al., 2007). Nevertheless, studies have confirmed that DMS-derived aerosol can be a significant source of CCN, especially in the remote marine atmosphere that receives little dust and aerosol from the continents (Ayers et al., 1991; Vallina et al., 2006), but the interactions and pathways in atmospheric DMS oxidation are complex and not fully understood, precluding quantitative modelling (Ayers et al., 1997). The view that emissions of DMS from the marine environment have implications for climate and atmospheric chemistry is widely supported, but there is as yet no unambiguous evidence for the validity of the CLAW hypothesis.

**Sources of DMS**

**Marine environment**

Various estimates of the flux of DMS to the atmosphere have been made (ranging from 15–109 Tg a\(^{-1}\)) but a review of the sources of DMS suggests that a figure of approximately 24.49±5.3 Tg a\(^{-1}\) should be adopted (Watts, 2000). The strength of the marine environment as a source of DMS has been estimated at around 21 Tg a\(^{-1}\) and, is therefore, by far the most important source, totalling around 80% of the total DMS flux, the remaining 20% originate from vegetation, salt marshes and estuaries, soils, wetlands, and also include anthropogenic sources (Watts, 2000). Dimethylsulfiniopropionate (DMSP) is the main source of DMS in the marine environment. DMSP is a metabolite of certain species of macroalgae (Challenger and Simpson, 1948; Van Alstyne and Puglisi, 2007) and phytoplankton, in particular in dinoflagellates and in species such as the Haptophytes *Emiliania huxleyi* and *Phaeocystis* (Liss et al., 1994; Malin and Kirst, 1997). Algae can accumulate DMSP to high internal concentrations reaching to hundreds of mM (reviewed in Stefels, 2000; Yoch, 2002). Corals and their zooxanthellae also contain large amounts of DMSP (Hill et al., 1995), which can be the source of high local DMS concentrations (approximately 1 μM) in coral reefs, for instance, in coral mucus ropes (Broadbent and Jones, 2004). It has been suggested that DMSP has a role as an osmolyte (Kiene et al., 2000; Stefels, 2000), an antifreeze compound (Kirst et al., 1991) or an antioxidant (Sunda et al., 2002), but its exact role remains unresolved and it is possible that it serves distinct roles in different organisms (Otte et al., 2004). Some vascular plants also contain DMSP, for instance, some halophytes of the genus *Spartina* and *Wollastonia biflora* contain significant amounts of DMS, and the molecule has also been detected in sugar cane (see Otte et al., 2004, for a review).

Upon lysis of DMSP-containing organisms, for instance, by viral attack (Malin et al., 1998) or zooplankton grazing (Wolfe et al., 1994; Wolfe and Steinke, 1996), DMS becomes dissolved in seawater. Microbial degradation of dissolved DMSP occurs through a number of different pathways (Howard et al., 2006; Johnston et al., 2008) (Fig. 2), and the majority of DMSP is not degraded to DMS (González et al., 1999; Kiene et al., 2000; Yoch 2002; Moran et al., 2003). Until recently, the enzyme cleaving DMSP was generally referred to as ‘DMSP lyase’, but the exact mechanisms by which DMS is formed from DMSP had not been investigated in any detail. Using genetic analysis of bacteria that form DMS from DMSP, Johnston and coworkers have described three different pathways of DMSP-dependent DMS formation that involve enzymes that are members of different enzyme families (Todd et al., 2007, 2009; Curson et al., 2008; Johnston et al., 2008).

Dissolved DMSP and/or DMS derived from it has been shown to be a powerful signalling molecule that attracts certain bacteria, for example, chemotaxis by *Silicibacter* TM1040 (Miller et al., 2004), but also affects the swimming
to text for references.

is oxidized to DMSO, for instance by DMS dehydrogenase. Refer to the ‘cleavage’ pathway, the responsible enzymes have been referred to as DMSP-lyases, but are in fact enzymes belonging to different protein families and exhibit different activities. These give rise to acrylate or 3-hydroxypropionate (3-HP). DMS can be oxidized by methyltransferases or DMS monooxygenases to methanethiol, or demethylated to methylmercapto-3-pionic acid (MPA), which can be either demethylated to mercaptopropionic acid (MMPA), which can be demethylated to acrylate or 3-hydroxypropionate (3-HP). DMS can be oxidized by methyltransferases or DMS monooxygenases to methanethiol, or is oxidized to DMSO, for instance by DMS dehydrogenase. Refer to text for references.

(c copepods, harbour seals, coral reef fish) and flying (petrels, shearwaters) behaviour of a range of organisms presumably as a foraging cue (see review by Johnston et al., 2008). A role of DMS as an info-chemical is also indicated by studies demonstrating that it allowed dogs and pigs to detect truffles in soil (Talou et al., 1990) and a study that showed the importance of volatile organic sulphur compounds including DMS, DMDS, and dimethyltrisulphide (DMTS) in the ‘bouquet of death’ that attracted burying beetles to carcasses of mice (Kalinová et al., 2009).

The majority of DMS emission is from open ocean environments, but microbial mats and intertidal sediments are also important sources of DMS (Steudler and Peterson, 1984). Several studies have investigated the cycling of DMS and related compounds in such ecosystems (Kiene and Capone, 1988; Kiene, 1988, 1990; Visscher et al., 1991, 2003; Jonkers et al., 1998; Lyimo et al., 2009). DMSP-producing plants and macroalgae, for example, the salt marsh cord grass *Spartina alterniflora* or the green algal seaweed *Ulva* spp., can contribute to the production of DMS in such ecosystems (Kiene and Capone, 1988, and references therein), however, other pathways of DMS formation may be more important in anoxic sediments, including the reduction of DMSO, the metabolism of sulphur-containing amino acids, and the methylation of sulphide (Kiene and Capone, 1988; Visscher et al., 1991, 2003; Jonkers et al., 1996; Lomans et al., 2001).

**Terrestrial sources of DMS**

DMS formation also occurs in terrestrial and freshwater environments, and, with exceptions (see below), DMS formation in these environments is not due to DMSP degradation. As noted above for coastal sediments, the processes involved are respiratory reduction of DMSO (Zinder and Brock, 1978c), degradation of sulphur-containing amino acids (Kadota and Ishida, 1972; Kiene and Capone, 1988), and anaerobic degradation of methoxylated aromatic compounds (Bak et al., 1992; Lomans et al., 2001). Methylation of sulphide in aerobic micro-organisms due to the action of thiol-S methyltransferase has been demonstrated and predominantly gives rise to MT (Drotar et al., 1987).

Overall, the emission of DMS from terrestrial and freshwater sources has not been studied as intensively as that from the marine environment and, as yet, there is not a clear view of the relative importance of different production mechanisms. Wetland emission rates of volatile sulphur compounds, including DMS, were subject to diel variations and an influence of plant communities was noted; in most wetlands, emission rates were insignificant compared to those measured in intertidal sediments dominated by *Spartina* (Cooper et al., 1989). *Sphagnum*-dominated peat bogs were shown to evolve both DMS and MT, the formation of both compounds was biological, and methylation of MT was the main source of DMS (Kiene and Hines, 1995). Soils may also emit volatile organic sulphur compounds, including DMS, and fluxes can be enhanced by waterlogging (Banwart and Brenner, 1976), but soils are not considered to be a major source of atmospheric sulphur (Andreae, 1990; Watts, 2000) and the volatilization of sulphur compounds is not thought to contribute significantly to the loss of sulphur from soils (Banwart and Brenner, 1976). Recently, DMS formation and degradation was observed in the deeper layers (mainly below 1 m depth) along the profile of an agricultural soil in Australia. The so-called agricultural sulphate soil investigated in that study is in close proximity to a tidal inlet, may receive sporadic inputs of seawater and thus is characterized by relatively high sulphate concentrations. It was suggested that DMS might be a potential source of the SO2 emissions that have been observed from this type of soils (Kinsela et al., 2007). The decomposition of plant residues in soil, especially those of crucifer species with a high content of sulphur-containing glucosinolates, can generate a number of volatile sulphur compounds including DMS, MT, and DMDS (Lewis and Papavizas, 1970). Such locally enhanced production of volatile sulphur compounds after the addition of crucifer residues to soils can be exploited in order to control soil-borne phytopathogenic fungi. The bio-fumigant effects of crucifer tissue addition were suggested to be mainly due to isothiocyanates and DMS was potent in inhibiting the activity of soil nitrifying bacteria (Bending and Lincoln, 2000).

In freshwater environments, DMS and MT production may occur in anoxic regions of stratified lakes and their sediments, as a result of sulphide methylation and/or the degradation of methoxylated aromatic compounds (Richards et al., 1991; Lomans et al., 1997, 2001; Fritz and Bachofen, 2000), but the production of DMS has also been

![Fig. 2. Major pathways of dimethylsulphoniopropionate (DMSP) degradation. DMSP can be demethylated to methylmercapto-propionic acid (MMPA), which can be either demethylated to mercaptopropionic acid (MPPA) or demethylated to acrylate. The pathway leading to DMS from DMSP is also known as the ‘cleavage’ pathway, the responsible enzymes have been referred to as DMSP-lyases, but are in fact enzymes belonging to different protein families and exhibit different activities. These give rise to acrylate or 3-hydroxypropionate (3-HP). DMS can be oxidized by methyltransferases or DMS monooxygenases to methanethiol, or demethylated to methylmercapto-3-pionic acid (MPA), which can be demethylated to acrylate or 3-hydroxypropionate (3-HP). DMS can be oxidized by methyltransferases or DMS monooxygenases to methanethiol, or is oxidized to DMSO, for instance by DMS dehydrogenase. Refer to text for references.](attachment://fig2.png)
detected in oxic layers of freshwater lakes (Richards et al., 1991). DMS in oxic freshwater lakes may be derived from phytoplankton and DMS release by phytoplankton cultures was stimulated by methionine (Caron and Kramer, 1994). Although DMSP is not generally considered to be a major DMS precursor in freshwater environments, DMS production in Lake Kinneret (Israel) appeared to be due to blooms of the DMSP-containing freshwater dinoflagellate *Peridinium gatunense* (Ginzburg et al., 1998). In a study of freshwater river sediments, Yoch and colleagues found that DMS was produced upon the addition of DMSP to sediment slurries and DMS-producing Gram-positive bacteria were identified (Yoch et al., 2001), demonstrating that the genetic potential for DMSP degradation was present far away from the marine environment, although it was noted by the authors that the enzyme systems responsible for DMS production could have cognate substrates other than DMSP.

**DMS production by plants**

Plants may be the main source of DMS in the terrestrial environment with a source strength estimated at 3.2 Tg a⁻¹, of which half is thought to be derived from tropical forests (Watts, 2000). Plants emit a range of volatile sulphur compounds including H₂S, DMS, MT, COS, and CS₂, with H₂S and DMS usually the dominant species, but emission rates are variable and dependent on many factors (reviewed by Schröder, 1993). In a study of environmental conditions that affect volatile sulphur emissions from plants, Fall and coworkers (Fall et al., 1988) showed that DMS was the dominant sulphur compound emitted by a range of crops including corn, alfalfa, and wheat. Sulphur fluxes were positively correlated with temperature and light intensity but were independent of the pCO₂ (Fall et al., 1988). A similar correlation of DMS emission rates and temperatures was found in a study of the gas exchange of DMS and COS of trees, but DMS emission was not a universal feature across the tree species tested and it was concluded that the contribution of tree-derived DMS to the global sulphur budget is negligible in temperate regions (Geng and Mu, 2006).

**Anthropogenic sources of DMS**

In an industrial context, DMS and other reduced sulphur compounds such as methanethiol, dimethyldisulphide (DMDS), and hydrogen sulphide are products in the wood-pulping process, for example, in the paper industry, and can occur in significant amounts in liquors of the so-called Kraft process where it is a by-product of the Swern oxidation of alcohols to aldehydes (Omura and Swern, 1978). The food and brewing industry, agriculture, and animal farming are also responsible for DMS emissions (Rappert and Müller, 2005; Kim et al., 2007). Anthropogenic sources of DMS are thought to be responsible for less than 1% of the total sources, but the emission of volatile sulphur compounds can be significant at the local scale. Due to the low odour thresholds of volatile organic sulphur compounds these can be a cause of nuisance odours (Zhu et al., 2002), for instance from wastewater treatment of paper manufacture (Catalan et al., 2008), or in the treatment of other sewage with high DMSO concentrations, caused by the reduction of DMSO to DMS under anaerobic conditions (Glinde mann et al., 2006). Industrial operations providing composts for mushroom production (Derix et al., 1990; Noble et al., 2001), field spreading of manure and the application of biosolids, as well as livestock operations are further DMS sources linked to the agriculture and farming industries (Rappert and Müller, 2005). DMS is also emitted from landfills, but is less abundant than hydrogen sulphide (Kim et al., 2005).

**Sinks for DMS and related compounds**

Given the role ascribed to DMS in affecting atmospheric chemistry and climate, it is of interest to understand the factors that control the flux of DMS to the atmosphere. In surface seawater the DMS concentration is determined by the rate of production (mainly) from DMSP, and a variety of loss terms. Sea-to-air transport is dependent on hydrological and meteorological parameters, for instance wind speed (Liss and Merlivat, 1986) and wave action (Watson et al., 1991). DMS is also photochemically oxidized in surface water to DMSO (Brimblecombe and Shooter, 1986). Although large quantities of DMS are produced in the upper mixed layer of the oceans, only a small fraction of DMS escapes to the atmosphere, while the majority (estimated at ~90%) is degraded in the mixed surface layer due to microbial processes, including its use either as a carbon or a sulphur source, or its biological degradation to DMSO (Kiene and Bates, 1990; Archer et al., 2002; Hatton et al., 2004). The micro-organisms and the microbial metabolism of DMS are discussed below.

**DMS-degrading micro-organisms**

The first insights into the microbiology of DMS-degrading organisms were obtained by studies of *Thiobacillus* and *Hyphomicrobium* species beginning in the 1970s with the isolation of *Thiobacillus* strains from a pine bark biofilter that was used to remove odorous compounds such as H₂S, MT, DMS, and DMDS from effluents of a paper pulp factory in Finland where these compounds were produced from methoxy groups of lignin in the paper-pulping process (Sivelä and Sundman, 1975). Further *Thiobacillus* species and isolates of *Hyphomicrobium* were then obtained that grew on DMS as a sole carbon source (De Bont et al., 1981; Kanagawa and Kelly, 1986; Suylen and Kuenen, 1986; Smith and Kelly, 1988; Pol et al., 1994). A diverse range of micro-organisms able to degrade DMS has since been isolated from a wide variety of environments, including soils, plant rhizospheres, activated sludge, biofiltration operations, seawater, cultures of marine algae, marine and freshwater sediments, microbial mats, and also humans...
from which DMS degraders have been isolated from feet and mouth samples. Table 2 lists species that have been shown to grow at the expense of DMS, while Fig. 3 illustrates the identity of DMS-degrading organisms in a phylogenetic context for representative strains with known 16S rRNA genes.

**Microbial metabolism of DMS**

There are numerous biological pathways that contribute to DMS degradation in the environment; in principal these serve (i) the utilization of DMS as a carbon and energy source, (ii) its oxidation to DMSO by phototrophic or heterotrophic organisms, and (iii) its utilization as a sulphur source. Various types of DMS degradation pathways have been reported in the literature, some of these featuring MT oxidase (Visscher and Taylor, 1993b), formaldehyde and methanethiol (De Bont et al., 1981). DMO has also been suggested to be responsible for methyl-tert butyl ether inhibition by chloroform while the DMS monooxygenase (DMO) was suggested to be inhibited by methyl-tert butyl ether in bacteria. Both the DMS monooxygenase and DMO pathways have not been forthcoming as it appeared to be unstable and no purification has been achieved. No genes encoding a DMS monooxygenase have been identified.

**Utilization of DMS as a carbon and energy source for bacterial growth.**

Utilization of DMS as a carbon and energy source is thought to occur by one of two pathways that have been suggested which contain either a DMS monooxygenase (De Bont et al., 1981) or a presumed methyltransferase (Visscher and Taylor 1993b) carrying out the initial oxidation of DMS. It has been suggested that the methyltransferase is inhibited by chloroform while the DMS monooxygenase was suggested to be inhibited by methyl-tert butyl ether (Visscher and Taylor 1993b).

**DMS monooxygenase pathway:** The work by De Bont and colleagues suggested that DMS metabolism in *Hyphomicrobium* S involved an initial NAD(P)H-dependent step of DMS oxidation by a DMS monooxygenase (DMO), yielding formaldehyde and methanethiol (De Bont et al., 1981). DMO has also been suggested to be responsible for initial DMS degradation in some *Thiobacillus* strains (Visscher and Taylor, 1993b). Formaldehyde is either directly assimilated into biomass or further oxidized via formate to CO₂ in order to provide reducing power. Assimilation of the formaldehyde produced during DMS and MT degradation in methylothrophic bacteria is accomplished by the serine or ribulose monophosphate cycles (De Bont et al., 1981; Anthony, 1982), while in DMS-degrading autotrophs that have been analysed formaldehyde is oxidized to CO₂, part of which is then assimilated into biomass via the Calvin–Benson–Bassham cycle (Kelly and Baker, 1990). Methanethiol produced by DMS monooxygenase in the first step is degraded by MT oxidase to formaldehyde, hydrogen peroxide, and sulphide (Suylen et al., 1987; Gould and Kanagawa, 1992). Formaldehyde is again either assimilated directly into biomass or oxidized to CO₂ while sulphide is converted to sulphite either by methanethiol oxidase (in the case of *Hyphomicrobium* spp.) or sulphide oxygenase (in the case of *Thiobacillus* spp.) which is then oxidized to sulphate (via sulphite oxidase). Hydrogen peroxide is reduced to water and oxygen by catalase and the growth on DMS of organisms utilizing MT oxidase is usually inhibited by the catalase inhibitor 3-amino-1,2,4-triazole.

The biochemistry and genetic basis of DMS and methanethiol degradation in these isolates has remained largely uncharacterized, although methanethiol oxidase was purified from several species including *Hyphomicrobium* EG (Suylen et al., 1987), *Thiobacillus thioparus* Tk-m (Gould and Kanagawa, 1992), and *Rhodococcus rhodochrous* (Kim et al., 2000). MT oxidase from *Hyphomicrobium* strain EG (Suylen et al., 1987) was reported not to require any cofactors for activity. The insensitivity of this MT oxidase towards the metal-chelating agents EDTA and neocuproine suggested that the enzyme did not contain metal ions or haem co-factors. It was suggested that the native *Hyphomicrobium* enzyme was a monomer with a molecular weight of 40–50 kDa, but MT oxidase from *Thiobacillus thioparus* sp. Tk-m (Gould and Kanagawa, 1992) appeared to be a monomer of 29–40 kDa. Two, more recent, studies reported the purification of MT oxidase from *Rhodococcus rhodochrous* (Kim et al., 2000) and a reassessment of the MT oxidase from *Thiobacillus thioparus* Tk-m (Lee et al., 2002), giving molecular weights for these enzymes of ~61 kDa. It is not clear whether different forms of methanethiol oxidase with different molecular weights may exist; in any case there is still a considerable lack of understanding of the biochemistry of methanethiol oxidation in bacteria.

Although the activity of DMS monooxygenase in methylotrophs and autotrophs degrading DMS under aerobic conditions was reported in a number of studies (De Bont et al., 1981; Borodina et al., 2000; Anesti et al., 2004, 2005; Moosvi et al., 2005), further information about the enzyme has not been forthcoming as it appeared to be unstable and no purification has been achieved. No genes encoding a DMS monooxygenase have been identified.

**Methyltransferase pathway:** *Thiobacillus* ASN-1 used an alternative initial step of DMS degradation which was independent of oxygen and which was suggested to be due to a methyltransferase (Visscher and Taylor, 1993b). It was suggested that the methyl group was transferred to an acceptor molecule and then further oxidized via folate-bound intermediates. The methyl accepting factor was suggested to be cobalamin-related although it was not identified (Visscher and Taylor, 1993a, b). Further oxidation of the remaining methanethiol appeared to follow the same scheme as in the DMS monooxygenase pathway described above.

**DMSO₂ and DMSO oxidation via DMS:** In the initial study of *Hyphomicrobium* X by De Bont and colleagues (De Bont et al., 1981), one of the substrates for growth of the strain...
Table 2. Bacterial isolates capable of growth on DMS as a sole source of carbon and energy

<table>
<thead>
<tr>
<th>Species</th>
<th>Strain</th>
<th>[$\text{DMS}]_{\text{max}}$</th>
<th>Isolated from</th>
<th>Isolation substrate (concentration)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Klebsiella pneumoniae</em></td>
<td>ATCC 9621</td>
<td>ND</td>
<td>Unknown (^2)</td>
<td>Unknown</td>
<td>Rammel and Zaffaroni, 1967</td>
</tr>
<tr>
<td><em>Thiobacillus</em> sp.</td>
<td>MS1</td>
<td>2.4 mM</td>
<td>Pinus sp. bark biofilter from a cellulose mill</td>
<td>DMS (1.6 mM)</td>
<td>Sivela and Sundman, 1975</td>
</tr>
<tr>
<td><em>Hyphomicrobium</em> sp.</td>
<td>S</td>
<td>ND</td>
<td>Soil (Wageningen, Netherlands)</td>
<td>DMSO (12.8 mM)</td>
<td>De Bont et al., 1981</td>
</tr>
<tr>
<td><em>Thiobacillus thioparus</em></td>
<td>Tk-m</td>
<td>2 mM</td>
<td>Activated sludge</td>
<td>Thiometon (6 mM)</td>
<td>Kanagawa et al., 1982; Kanagawa and Kelly, 1986</td>
</tr>
<tr>
<td><em>Hyphomicrobium</em> sp.</td>
<td>EG</td>
<td>0.1 mM</td>
<td>Papermill biofilter</td>
<td>DMSO (10 mM)</td>
<td>Suylen and Kuenen, 1986</td>
</tr>
<tr>
<td><em>Thiobacillus</em> sp.</td>
<td>E1</td>
<td>2 mM</td>
<td>Commercial peat</td>
<td>DMS (2 mM)</td>
<td>Smith, 1987</td>
</tr>
<tr>
<td><em>Thiobacillus</em> sp.</td>
<td>E3</td>
<td>2 mM</td>
<td>Garden compost</td>
<td>DMS (2 mM)</td>
<td>Smith, 1987</td>
</tr>
<tr>
<td><em>Thiobacillus</em> sp.</td>
<td>E4</td>
<td>2 mM</td>
<td>Cattle manure</td>
<td>DMS (2 mM)</td>
<td>Smith, 1987</td>
</tr>
<tr>
<td><em>Thiobacillus</em> sp.</td>
<td>E5</td>
<td>2 mM</td>
<td>Marine mud (Plymouth, UK)</td>
<td>DMS (2 mM)</td>
<td>Smith, 1987</td>
</tr>
<tr>
<td><em>Thiobacillus</em> sp.</td>
<td>E7</td>
<td>2 mM</td>
<td>Sphagnum sp. moss from a deodorization unit</td>
<td>DMS (2 mM)</td>
<td>Smith, 1987</td>
</tr>
<tr>
<td><em>Thiobacillus thioparus</em></td>
<td>E6</td>
<td>2 mM</td>
<td>Pond water (Coventry, UK)</td>
<td>DMDS (2 mM)</td>
<td>Smith and Kelly, 1988</td>
</tr>
<tr>
<td><em>Hyphomicrobium</em> sp.</td>
<td>I55</td>
<td>ND</td>
<td>Peat biofilter</td>
<td>DMS (1 mM)</td>
<td>Zhang et al., 1991a</td>
</tr>
<tr>
<td><em>Thiobacillus thioparus</em></td>
<td>DW44</td>
<td>ND</td>
<td>Peat biofilter</td>
<td>Thiosulphate (20 mM)</td>
<td>Cho et al., 1991</td>
</tr>
<tr>
<td><em>Thiobacillus</em> sp.</td>
<td>K4</td>
<td>ND</td>
<td>Biofilter</td>
<td>CS$_2$</td>
<td>Peas et al., 1991</td>
</tr>
<tr>
<td><em>Thiobacillus</em> sp.</td>
<td>T5</td>
<td>1.3 mM</td>
<td>Marine microbial mat (Texel, Netherlands)</td>
<td>Thiosulphate (10 mM)</td>
<td>Visscher et al., 1991</td>
</tr>
<tr>
<td><em>Thiobacillus</em> sp.</td>
<td>ANS-1</td>
<td>ND</td>
<td>Tidal sediment (Georgia, USA)</td>
<td>DMS (0.5 mM)</td>
<td>Visscher and Taylor, 1993b</td>
</tr>
<tr>
<td><em>Hyphomicrobium</em> sp.</td>
<td>VS</td>
<td>1 mM</td>
<td>Activated sludge</td>
<td>DMS (15 µM)</td>
<td>Pol et al., 1994</td>
</tr>
<tr>
<td><em>Desulfitotomaculum</em> sp.</td>
<td>TDS2</td>
<td>ND</td>
<td>Thermophilic fermenter sludge</td>
<td>DMS (5 mM) and 10 mM sulphate</td>
<td>Tanimoto and Bak, 1994</td>
</tr>
<tr>
<td><em>Desulfitotomaculum</em> sp.</td>
<td>SDN4</td>
<td>ND</td>
<td>Thermophilic fermenter sludge</td>
<td>DMS (5 mM) and 5 mM nitrate</td>
<td>Tanimoto and Bak, 1994</td>
</tr>
<tr>
<td><em>Methylphaga sulfidovorans</em></td>
<td>RB-1</td>
<td>2.4 mM</td>
<td>Marine microbial mat (Texel, Netherlands)</td>
<td>DMS (1.5 mM)</td>
<td>de Zwart et al., 1996</td>
</tr>
<tr>
<td><em>Hyphomicrobium</em> sp.</td>
<td>MS3</td>
<td>2.4 mM</td>
<td>Garden soil (Ghent, Belgium)</td>
<td>DMS/DMDS (1.4/1.1 mM)</td>
<td>Smet et al., 1996</td>
</tr>
<tr>
<td><em>Xanthobacter tagelidis</em></td>
<td>TagT2C</td>
<td>2.5 mM</td>
<td>Tagetes patula rhizosphere</td>
<td>72Cl(2.5 mM)</td>
<td>Padden et al., 1997</td>
</tr>
<tr>
<td><em>Pseudonocardia asacharolytica</em></td>
<td>580</td>
<td>ND</td>
<td>Animal rendering plant biofilter</td>
<td>DMS (1 mM)</td>
<td>Reichert et al., 1998</td>
</tr>
<tr>
<td><em>Pseudonocardia sulfidoxydans</em></td>
<td>592</td>
<td>ND</td>
<td>Animal rendering plant biofilter</td>
<td>DMS (0.5 mM)</td>
<td>Reichert et al., 1998</td>
</tr>
<tr>
<td><em>Starkeya novellac</em></td>
<td>SRM</td>
<td>ND</td>
<td>Sewage (Kwangju, South Korea)</td>
<td>Thiosulphate (63 mM)</td>
<td>Cha et al., 1999</td>
</tr>
<tr>
<td><em>Thiocapsa</em></td>
<td>M11</td>
<td>1 mM</td>
<td>Marine microbial mat (Mellum, Germany)</td>
<td>Sulphide (1.6 mM)</td>
<td>Jonkers et al., 1999</td>
</tr>
<tr>
<td><em>roseopseudonsia</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Methylobacterium podarium</em></td>
<td>FM1</td>
<td>ND</td>
<td>Homo sapiens foot</td>
<td>MMA (20 mM)</td>
<td>Vohra, 2000</td>
</tr>
<tr>
<td><em>Hyphromicrobium sulfonivorans</em></td>
<td>S1</td>
<td>ND</td>
<td>Garden soil (Warwickshire, UK)</td>
<td>DMSO$_2$ (10 mM)</td>
<td>Borodina et al., 2002</td>
</tr>
<tr>
<td><em>Arthrobacter sulfonivorans</em></td>
<td>ALL/A</td>
<td>ND</td>
<td>Allium aflatunense rhizosphere</td>
<td>DMSO$_2$ (10 mM)</td>
<td>Borodina et al., 2002</td>
</tr>
<tr>
<td><em>Arthrobacter sulfonivorans</em></td>
<td>ALL/B</td>
<td>ND</td>
<td>Allium aflatunense rhizosphere</td>
<td>DMSO$_2$ (10 mM)</td>
<td>Borodina et al., 2002</td>
</tr>
<tr>
<td><em>Arthrobacter methylotrophus</em></td>
<td>TGA</td>
<td>ND</td>
<td>Tagetes minuta rhizosphere</td>
<td>DMSO$_2$ (10 mM)</td>
<td>Borodina et al., 2002</td>
</tr>
<tr>
<td><em>Methylbacterium podarium</em></td>
<td>FM4</td>
<td>1 mM</td>
<td>Homo sapiens foot</td>
<td>MMA (20 mM)</td>
<td>Anesti et al., 2004</td>
</tr>
<tr>
<td><em>Hyphromicrobium sulfonivorans</em></td>
<td>CT</td>
<td>ND</td>
<td>Homo sapiens teeth</td>
<td>DMS (1 mM)</td>
<td>Anesti et al., 2005</td>
</tr>
<tr>
<td><em>Hyphromicrobium sulfonivorans</em></td>
<td>DTg</td>
<td>ND</td>
<td>Homo sapiens tongue</td>
<td>DMS (1 mM)</td>
<td>Anesti et al., 2005</td>
</tr>
<tr>
<td><em>Methylbacterium thioconatum</em></td>
<td>MM4</td>
<td>ND</td>
<td>Homo sapiens tongue</td>
<td>MMA (20 mM)</td>
<td>Anesti et al., 2005</td>
</tr>
<tr>
<td><em>Methylbacterium extorquens</em></td>
<td>MM9</td>
<td>ND</td>
<td>Homo sapiens tongue</td>
<td>Methionine (5 mM)</td>
<td>Anesti et al., 2005</td>
</tr>
<tr>
<td><em>Methylbacterium sp.</em></td>
<td>MM10</td>
<td>ND</td>
<td>Homo sapiens tongue</td>
<td>Cysteine (5 mM)</td>
<td>Anesti et al., 2005</td>
</tr>
<tr>
<td><em>Micrococcus luteus</em></td>
<td>MM7</td>
<td>ND</td>
<td>Homo sapiens teeth</td>
<td>MMA (20 mM)</td>
<td>Anesti et al., 2005</td>
</tr>
<tr>
<td><em>Bacillus licheniformis</em></td>
<td>3S(b)</td>
<td>ND</td>
<td>Homo sapiens gingvae</td>
<td>DMS (1 mM)</td>
<td>Anesti et al., 2005</td>
</tr>
<tr>
<td><em>Bacillus licheniformis</em></td>
<td>2Tgb</td>
<td>ND</td>
<td>Homo sapiens tongue</td>
<td>DMS (1 mM)</td>
<td>Anesti et al., 2005</td>
</tr>
<tr>
<td><em>Brevibacterium casei</em></td>
<td>3Tg</td>
<td>ND</td>
<td>Homo sapiens tongue</td>
<td>DMS (1 mM)</td>
<td>Anesti et al., 2005</td>
</tr>
<tr>
<td><em>Brevibacterium casei</em></td>
<td>3S(a)</td>
<td>ND</td>
<td>Homo sapiens gingvae</td>
<td>DMS (1 mM)</td>
<td>Anesti et al., 2005</td>
</tr>
<tr>
<td><em>Mycobacterium fluoranthennivorans</em></td>
<td>DSG3</td>
<td>ND</td>
<td>River sediment (London, UK)</td>
<td>DMA (10 mM)</td>
<td>Boden, 2005; Boden et al., 2008</td>
</tr>
</tbody>
</table>
### Table 2. Continued

<table>
<thead>
<tr>
<th>Species</th>
<th>Strain</th>
<th>[DMS](_{\text{MAX}})</th>
<th>Isolated from</th>
<th>Isolation substrate (concentration)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylophaga sp.</td>
<td>DMS001</td>
<td>ND</td>
<td>Emiliania huxleyi culture</td>
<td>DMS (50 μM)</td>
<td>Schäfer, 2007</td>
</tr>
<tr>
<td>Methylophaga sp.</td>
<td>DMS002</td>
<td>ND</td>
<td>Emiliania huxleyi culture</td>
<td>DMS (50 μM)</td>
<td>Schäfer, 2007</td>
</tr>
<tr>
<td>Methylophaga sp.</td>
<td>DMS003</td>
<td>ND</td>
<td>Emiliania huxleyi culture</td>
<td>DMS (50 μM)</td>
<td>Schäfer, 2007</td>
</tr>
<tr>
<td>Methylophaga sp.</td>
<td>DMS004</td>
<td>ND</td>
<td>Emiliania huxleyi culture</td>
<td>DMS (50 μM)</td>
<td>Schäfer, 2007</td>
</tr>
<tr>
<td>Methylophaga sp.</td>
<td>DMS007</td>
<td>ND</td>
<td>Emiliania huxleyi culture</td>
<td>DMS (50 μM)</td>
<td>Schäfer, 2007</td>
</tr>
<tr>
<td>Methylophaga sp.</td>
<td>DMS009</td>
<td>ND</td>
<td>Emiliania huxleyi culture</td>
<td>DMS (50 μM)</td>
<td>Schäfer, 2007</td>
</tr>
<tr>
<td>Methylophaga sp.</td>
<td>DMS010</td>
<td>ND</td>
<td>Emiliania huxleyi culture</td>
<td>DMS (50 μM)</td>
<td>Schäfer, 2007</td>
</tr>
<tr>
<td>Methylophaga thiooxidans(d)</td>
<td>DMS011</td>
<td>ND</td>
<td>Emiliania huxleyi culture</td>
<td>DMS (50 μM)</td>
<td>Schäfer, 2007</td>
</tr>
<tr>
<td>Methylophaga sp.</td>
<td>DMS021</td>
<td>ND</td>
<td>Rock pool water (Coral Beach, UK)</td>
<td>DMS (50 μM)</td>
<td>Schäfer, 2007</td>
</tr>
<tr>
<td>Methylophaga sp.</td>
<td>DMS026</td>
<td>ND</td>
<td>Sea water (English channel)</td>
<td>DMS (50 μM)</td>
<td>Schäfer, 2007</td>
</tr>
<tr>
<td>Methylophaga sp.</td>
<td>DMS039</td>
<td>ND</td>
<td>Sea water (Achmelvich, UK)</td>
<td>DMS (50 μM)</td>
<td>Schäfer, 2007</td>
</tr>
<tr>
<td>Methylophaga sp.</td>
<td>DMS040</td>
<td>ND</td>
<td>Sea water (Achmelvich, UK)</td>
<td>DMS (50 μM)</td>
<td>Schäfer, 2007</td>
</tr>
<tr>
<td>Methylophaga sp.</td>
<td>DMS043</td>
<td>ND</td>
<td>Sea water (Achmelvich, UK)</td>
<td>DMS (50 μM)</td>
<td>Schäfer, 2007</td>
</tr>
<tr>
<td>Methylophaga sp.</td>
<td>DMS044</td>
<td>ND</td>
<td>Sea water (Achmelvich, UK)</td>
<td>DMS (50 μM)</td>
<td>Schäfer, 2007</td>
</tr>
<tr>
<td>Methylophaga sp.</td>
<td>DMS048</td>
<td>ND</td>
<td>Rock pool water (Coral Beach, UK)</td>
<td>DMS (50 μM)</td>
<td>Schäfer, 2007</td>
</tr>
<tr>
<td>Methylophaga sp.</td>
<td>MP(e)</td>
<td>ND</td>
<td>Sea water (Mokpo, South Korea)</td>
<td>Methanol (220 mM)</td>
<td>Kim et al., 2007</td>
</tr>
<tr>
<td>Hyphomicrobium facile</td>
<td>–</td>
<td>ND</td>
<td>Marsh sediment (De Bruuk, Netherlands)</td>
<td>DMS (50 μM)</td>
<td>Haaijer et al., 2008</td>
</tr>
<tr>
<td>Microbacterium sp.</td>
<td>NTUT26</td>
<td>ND</td>
<td>Wastewater sludge from a wood pulp factory (Taiwan)</td>
<td>DMS (1.6 mM)</td>
<td>Shu and Chen, 2009</td>
</tr>
<tr>
<td>Desulforosarcina sp.</td>
<td>SD1</td>
<td>ND</td>
<td>Mangrove sediment (Tanzania)</td>
<td>DMS (initially 20 μM, additions rising to 100 μM)</td>
<td>Lyimo et al., 2009</td>
</tr>
</tbody>
</table>

\(a\) ‘Aerobacter aerogenes’.  
\(b\) Isolation details of this strain do not appear in the literature.  
\(c\) ‘Thiobacillus novellus’.  
\(d\) ‘Methylophaga sp. DMS010’.  
\(e\) ‘Methylophaga aminosulfidovorans’.

DMA, dimethylamine; MMA, monomethylamine; ND, not determined; T2C, thiophene-2-carboxylate.

### Table 3. Bacterial isolates that are capable of oxidizing DMS to DMSO

<table>
<thead>
<tr>
<th>Species</th>
<th>Strain</th>
<th>Isolated from</th>
<th>Isolation substrate</th>
<th>Metabolism producing DMSO</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiocystis sp.</td>
<td>A</td>
<td>Salt Pond (MA, USA)</td>
<td>Sulphide</td>
<td>Anoxogenic phototrophic growth (DMS as electron-donor)</td>
<td>Zeyer et al., 1987</td>
</tr>
<tr>
<td>Delftia acidovorans</td>
<td>DMR-11</td>
<td>Peat biofilter</td>
<td>Peptone</td>
<td>Anaerobic heterotrophic growth (co-oxidation)</td>
<td>Zhang et al., 1991b</td>
</tr>
<tr>
<td>Nitrosomonas europaea</td>
<td>ATCC 19178(d)</td>
<td>Unknown</td>
<td>Unknown</td>
<td>Aerobic ammonium oxidation (co-oxidation)</td>
<td>Juliette et al., 1993</td>
</tr>
<tr>
<td>Methylococcus pelagicum</td>
<td>NI</td>
<td>Seawater (Japan)</td>
<td>Methane</td>
<td>Aerobic methane oxidation (co-oxidation)</td>
<td>Fuse et al., 1998</td>
</tr>
<tr>
<td>Sagittula stellata</td>
<td>E-37</td>
<td>Seawater enrichment culture on high molecular weight fraction of pulp mill effluent</td>
<td>Yeast extract/tryptone</td>
<td>Aerobic heterotrophic growth (co-oxidation)</td>
<td>Gonzalez et al., 1997</td>
</tr>
<tr>
<td>Rhodovulum sulfidophilum</td>
<td>SH1</td>
<td>Seawater</td>
<td>Bicarbonate</td>
<td>Anoxogenic phototrophic growth (DMS as electron-donor)</td>
<td>Hanlon et al., 1994</td>
</tr>
<tr>
<td>Acinetobacter sp.</td>
<td>20B</td>
<td>Soil (Japan)</td>
<td>Succinate</td>
<td>Heterotrophic growth (utilization of DMS as sulphur source)</td>
<td>Horinouchi et al., 1997</td>
</tr>
<tr>
<td>Thiocapsa roseopersicina</td>
<td>M1</td>
<td>Marine microbial mat (Mellum, Germany)</td>
<td>Sulphide</td>
<td>Anoxogenic phototrophic growth (DMS as electron-donor)</td>
<td>Visscher and van Gemerden, 1991</td>
</tr>
</tbody>
</table>

\(d\) The online catalogue of the American Type Culture Collection does not list a strain with this accession number (5 November 2009), however, there is a Nitrosomonas europaea ATCC 19718.
was DMSO, which was reduced to DMS and thus fed into the DMS monooxygenase pathway. Subsequently, it was shown that DMSO could also be degraded by some methylotrophs via DMS, as enzyme activities for DMSO reductase, DMSO reductase, and DMS monooxygenase were detected in cell-free extracts of *Hyphomicrobium sulfonivorans* and *Arthrobacter sulfonivorans* growing on these compounds (Borodina et al., 2000, 2002).

**Growth on DMS under anoxic conditions**

Several bacterial and archaeal strains able to degrade DMS and MT under anoxic conditions have been isolated (Kiene et al., 1986; Ni and Boone, 1991; Finster et al., 1992; Visscher and Taylor, 1993; Tanimoto and Bak, 1994; Lomans et al., 1999; Lyimo et al., 2000). The thermodynamic aspects of growth of SRB and methanogens on methylated sulphur compounds have been reviewed in detail elsewhere (Scholten et al., 2003). SRB and methanogens are thought to be responsible for anaerobic DMS oxidation in anoxic sediments of coastal salt marshes, estuaries, and freshwater sediments (Zinder and Brock, 1978; Kiene et al., 1986; Kiene and Capone, 1988; Lomans et al., 1999; Lyimo et al., 2000). The characteristics of methanogenic Archaea growing on DMS and MT have been reviewed previously, with isolates belonging to the genera *Methanolobus*, *Methanomethylovorans*, *Methanosarcina*, and

---

**Fig. 3.** Phylogenetic tree depicting the genetic diversity of bacterial isolates capable of assimilating carbon from DMS (overlaid in pink) or degrading DMS to DMSO (green). The tree is based on an alignment of small subunit ribosomal RNA gene sequences and was derived using the Neighbor–Joining option in MEGA4. Bootstrap values are of 100 replicates.

**Fig. 4.** Scheme showing the biochemical and chemical interconversions of C1-sulphur compounds and key intermediates in carbon and sulphur metabolism that have been observed across a wide range of micro-organisms (refer to Table 1 for chemical formulae of the C1-sulphur compounds). Either the enzymes/processes or an organism in which the conversion has been observed are given as an example (for further detail refer to text). 1, MSA monooxygenase; 2, FMNH2-dependent DMSO2 monooxygenase (Endoh et al., 2005); 3, DMSO2 dehydrogenase; 4, *Rhodococcus* SY1 (Omori et al., 1995); 5, DMSO reductase; 6, DMS dehydrogenase; 7, DMS monooxygenase/DMS methyltransferase; 8, methylation of MT; 9, chemical oxidation of MT to DMDS; 10, DMDS reductase (Smith and Kelly, 1988); 11, MT oxidase; 12, bacterial inorganic sulphur oxidation pathways; 13, sulphite oxidase; 14, formaldehyde oxidation (various enzymes); 15, formate dehydrogenase; 16, Calvin–Benson–Bassham cycle; 17, serine cycle or ribulose monophosphate cycle.
Methanosalsus (Lomans et al., 2002). Compared to methanogens, relatively few SRB growing on DMS have been isolated. Tanimoto and Bak (1994) obtained Gram positive, spore-forming SRB from thermophilic fermenter sludge which they classified as Desulfotomaculum species. These isolates were also able to grow on DMS using nitrate as electron acceptor (Tanimoto and Bak, 1994). Based on slurry incubations with tungstate and bromoethanesulphonate addition selectively to inhibit SRB and methanogens, respectively, Lyimo and coworkers found that the degradation of DMS and MT in anoxic mangrove sediments was dominated by SRB (Lyimo et al., 2009). A strain was isolated, the first SRB from a marine environment, which was closely related to Desulfosaccrina sp. and exhibited very slow growth rates on DMS, but which had a high affinity for DMS. The authors concluded that, due to the extremely slow growth observed, such SRB might be outcompeted by methanogens in enrichments and slurry incubations when relatively high DMS concentrations are used, since methane production increased exponentially during slurry incubations.

The biochemical and genetic basis of DMS degradation in SRB remains uncharacterized. More data are available for methanogens. It was shown that, during growth on acetate of the methanogen Methanosarcina barkeri, the cells also converted DMS and methylmercaptopropionate (MMPA) to methane and a corrinoid protein functioned as a co-enzyme M methylase capable of DMS and MMPA degradation (Tallant and Krzycki, 1997). Fused corrinoid/methyl transfer proteins have been implicated in methyl sulphide metabolism in Methanosarcina acetivorans (Oelgeschlaeger and Rother, 2009).

Oxidation of DMS to DMSO

In phototrophic bacteria, the oxidation of DMS to DMSO can be used to provide electron donors for carbon dioxide fixation as suggested by a study of DMS degradation by a culture of an anoxygenic phototrophic purple sulphur bacterium that converted DMS stoichiometrically to DMSO (Zeyer et al., 1987). Similarly, DMS can be utilized by certain phototrophic green sulphur bacteria when growing on reduced sulphur compounds such as thiosulphate and hydrogen sulphide (Vogt et al., 1997).

DMS to DMSO conversion by heterotrophic bacteria was first described by Zhang et al. (1991b) in Pseudomonas acidovorans DMR-11 (reclassified as Delfta acidovorans). In this strain DMSO was stoichiometrically formed from DMS as a product of co-oxidation during heterotrophic metabolism, for instance, during growth on a range of organic compounds, but no carbon from DMS was assimilated. DMS removal in cell-free extracts of strain DM-11 was dependent on the presence of NADPH, which could not be replaced by NADH. Complete conversion of DMS to DMSO was also shown in the marine heterotrophic bacterium Saggittula stellata E-37 (González et al., 1997) in cells grown on glucose, irrespective of additional organic carbon being added during the assay. The enzymes responsible for the conversion of DMS to DMSO in both Saggittula stellata and Delfta acidovorans are unknown.

DMS dehydrogenase: The biochemistry and genetics of DMS to DMSO oxidation in phototrophic metabolism in which DMS serves as an H donor have been studied in detail in Rhodovulum sulfidophilum (Hanlon et al., 1996; McDevitt et al., 2002). In this strain, DMS-dependent DMSO formation is mediated by DMS dehydrogenase (DMSDH), a heterotrimeric enzyme comprising three subunits (DdhABC) in which a molybdopterin co-factor is bound to the A subunit (Hanlon et al., 1996). The enzyme is encoded by the dhd operon containing the genes dhdABC, which encode the A, B (containing putative [Fe-S] clusters) and C (containing a b-type haem) subunits, and dhdD is thought to encode a polypeptide that could be responsible for the maturation of the molybdopterin-containing enzyme (McDevitt et al., 2002).

Oxidation of DMS to DMSO by methanotrophs and nitrifying bacteria: DMS oxidation has also been observed in resting cell suspensions of methane-grown methanotrophic isolates of Methylocibrium (Fuse et al., 1998; Sorokin et al., 2000) and in Methylocubrium pelagicum the product was identified as DMSO. The nitrifying bacteria Nitrosomonas europaea and Nitrosooccus oceani (Juliette et al., 1993) also converted DMS to DMSO and some evidence suggests that ammonia monoxygenase (AMO) is the enzyme co-oxidizing DMS to DMSO in these bacteria. While the co-oxidation of MT by purified methane monoxygenase (MMS), the key enzyme in aerobic methanotrophic bacteria, has been reported (Colby et al., 1977), it is still unclear whether DMS is co-oxidized by MMO, although this seems likely given the close evolutionary relationship of AMO and particulate MMO (Holmes et al., 1995).

Reduction of DMSO to DMS by DMSO reductase: A range of micro-organisms can couple the oxidation of organic carbon compounds to respiratory reduction of DMSO to DMS under anoxic conditions (Zinder and Brock, 1978a). The enzyme dimethylsulphoxide reductase, which reduces DMSO to DMS, was first purified and characterized from Rhodobacter sphaeroides. In this strain, it is a soluble periplasmic single subunit enzyme of 82 kDa that contains a molybdopterin co-factor (Satoh and Kurihara, 1987), which can also reduce trimethylamine oxide (Styrvold and Strom, 1984). It is encoded by the gene dmsA (Yamamoto et al., 1995). A similar enzyme was purified from Rhodobacter capsulatus (McEwan et al., 1991). The DMSO reductase in E. coli is rather different. It is a heterotrimeric enzyme expressed under anaerobic conditions, which is anchored in the periplasmic membrane. It is encoded by the operon dmsABC (Bilous et al., 1988), in which the genes encode the active catalytic subunit DmsA (82 kDa) that contains the molybdenopterin co-factor, an electron transfer protein DmsB (23.6 kDa), and a membrane anchor DmsC (22.7 kDa) (Sambasivarao et al., 1990). Despite the
differences in enzyme structure, the catalytic subunits of *R. sphaeroides* and *E. coli* share 29% sequence identity at the amino acid level (Yamamoto et al., 1995). In *Hyphomicrobium sulfonivorans* a membrane-bound DMSO reductase that reduced DMSO to DMS was expressed during aerobic growth on DMSO₂, thus not having a role in anaerobic respiration under these conditions. Only a weak cross-reaction was reported for the immunoblotting of *H. sulfonivorans* membrane fraction with an antibody against the *R. capsulatus* enzyme (Borodina et al., 2002). The observation that DMSO reductase activity was present in the membrane fraction would suggest that it might be similar to the *E. coli* type DMSO reductase, but that it is regulated differently to the *E. coli* enzyme.

DMSO reductase may carry out the reverse reaction in which DMS is oxidised to DMSO, so it might be a candidate for DMS degradation in the environment. However, although the enzyme from *R. capsulatus* can carry out the reverse reaction *in vitro*, its *Kₘ* for DMS is high (1 mM) and DMSO strongly inhibits this reaction (Adams et al., 1999), so it would appear unlikely to be relevant under physiological conditions. The *E. coli* enzyme is expressed constitutively under anaerobic conditions (Weiner et al., 1992). Overall, at this point there is little support in the suggestion that DMSO reductases could provide a route of DMS degradation in, for instance, theoxic mixed surface layer of the oceans.

**Assimilation of C¹ sulphur compounds as a sulphur source**

In addition to serving as a substrate for the growth of aerobic and anaerobic micro-organisms, DMSO and DMS can also be used as a source of sulphur. A strain of *Marinobacter* was able to utilize DMS as a sulphur source with the aid of light, probably using a flavoprotein (Fuse et al., 2000). *Pseudomonas aeruginosa* can grow with methanesulphonate as a sole sulphur source, using the flavin-linked methanesulphonate monooxygenase MsuED (Kertesz et al., 1999) that is repressed by sulphide, sulphite, and sulphate. It is closely related to the alkanesulphonate monooxygenase (SsuED) that is induced during the sulphate-starvation response in *E. coli* (Eichhorn et al., 1999). Bacterial sulphur assimilation by these enzymes has been reviewed in detail (Kertesz, 2000). In a strain of *Acinetobacter*, DMS degradation via DMSO which led to the assimilation of sulphur was observed. The enzyme oxidizing DMS to DMSO was related to multi-component monooxygenases oxidizing toluene and similar substrates. It was termed DMS monooxygenase by the authors (Horinouchi et al., 1997), but this is inappropriate as the degradation of DMS by this enzyme does not generate MT and formaldehyde. Similarly *Rhodococcus* strain SY1 utilized DMS, DMSO, and DMSO₂ as sulphur sources and, in both strains, the sequence of oxidation started with DMS oxidation to DMSO which was oxidized to DMSO₂ and further to MSA (Omori et al., 1995). Work on *Pseudomonas putida* DS1 suggested the latter was then a substrate for a SsuED type enzyme (Endoh et al., 2003).

**M.SA catabolism**

A different kind of methanesulphonate monooxygenase exists in methylotrophic bacteria such as *Methylosulphononas methylivorans* which can grow on MSA as a sole source of carbon and energy (Kelly and Murrell, 1999). Its MSA monooxygenase is composed of four distinct polypeptides. The hydroxylase subunit was composed of a 48 kDa and 20 kDa subunits making up a native protein of around 210 kDa of a α3β3 structure. Further components were identified as a ferredoxin (32 kDa) and a reductase (38 kDa). The enzyme subunits are encoded by the genes *msmAEGH* (De Marco et al., 1999) and the closely linked *msmEFGH* operon encodes proteins involved in transport of MSA (Jamshad et al., 2006). Transcriptional analysis showed that *msmEFGH* operon was expressed constitutively while *msmAEGH* was induced by MSA (Jamshad et al., 2006).

**Ecology of micro-organisms degrading DMS and related compounds**

Early studies suggested that micro-organisms catabolizing DMS mainly belonged to the genera *Hyphomicrobium*, *Thiobacillus*, and additional isolation studies have significantly extended the range of organisms able to grow on DMS (Table 1). In addition to the shortcomings of microbial community analyses by cultivation-dependent approaches, there are particular difficulties that are often encountered in the isolation of DMS-degrading bacteria (Suylen and Kuenen, 1986; Smith and Kelly, 1988). The diversity of cultivable DMS-oxidizing bacteria still precludes the delineation of major patterns in their distribution. It is almost certain that the true extent of the phylogenetic diversity of DMS-degrading organisms has not yet been identified, either because organisms are recalcitrant to culturing conditions or due to the capacity to degrade DMS being a phenotypic trait that is only rarely tested, even in studies of methylotrophic bacteria. This is most likely due to the low attraction of working with this smelly compound. The ability to degrade DMS is usually not conserved among closely related species, i.e. there is no perfect correlation of phytype and phenotype. This largely negates the direct application of the widely used cultivation-independent ribosomal RNA approach for studying DMS-degrading microbial populations in the environment. Nevertheless, some investigations on relevant environments, using 16S rRNA genes as markers have shown the presence of microbial populations that might degrade DMS, based on their relatedness to known DMS-degrading strains. For example, bacteria were found in marine DMS enrichment cultures (Vila-Costa et al., 2006) that were related to marine DMS degrading *Methylophaga* isolates (Schäfer, 2007). Also, populations of related bacteria were detected in stable
isotope probing experiments with $^{13}$C-DMS following a DMSP-producing phytoplankton bloom of *Emiliania huxleyi* in the English Channel (Neufeld et al., 2008). Further application of SIP will allow improved definition of the phylogenetic diversity of DMS-degrading microbial populations in environmental samples, but the approach can only detect those organisms that assimilate the carbon from DMS. Additional tools that target key enzymes of DMS metabolism will therefore be required to map the diversity and activity of DMS degrading micro-organisms. This will require new insights into the metabolism of DMS at a molecular level, including studying the biochemistry and genetics of suitable model organisms in order to obtain a detailed understanding of the enzymes and genes underpinning DMS degradation across a range of isolates. Molecular methods targeting functional genes of DMS metabolism will not only allow the elucidation of patterns in the distribution of DMS-degrading micro-organisms in nature, independent of cultivation, but will also highlight particular microbial populations for targeted isolation. Studying environmentally relevant model organisms in more detail should also be useful in delineating the physiological response of DMS-degrading micro-organisms and their potential to degrade DMS under varying environmental conditions. Many of the known DMS-degrading bacteria (Table 2) are able to grow on a range of substrates. DMS-degrading *Methylophaga* species, for instance, grow on methanol and methylated amines (De Zwart et al., 1996; Schäfer, 2007), two compounds which are present in the marine environment in concentrations as high as 50–250 nM in the case of methanol in the tropical Atlantic (Williams et al., 2004). These concentrations are similar to or exceed those of DMS which are typically in the low nanomolar range (Kettle et al., 1999). Being presented with more than one growth substrate may have important effects and the physiological and transcriptional responses of DMS-degrading organisms under such conditions require further study.

**Interactions of DMS-degrading micro-organisms and plants**

The focus of most research on the synthesis and catabolism of DMS has been on the marine system. There is some evidence for the production of DMS and other volatile sulphur species by plants, but there are few data on emissions from vegetation in temperate and boreal regions (Watts, 2000). The association with plants of microbial populations degrading DMS and related compounds is therefore of particular interest for future study. Above-ground interactions of plants and bacteria occur in the phyllosphere, which is the site of volatile sulphur emission. It has been shown previously that plants harbour diverse populations of epiphytic and endophytic *Methylobacterium* species (Abanda-Nkwatt et al., 2006; Knief et al., 2008), which are thought to thrive on methanol released from pectin metabolism in the cell wall (Galbally and Kirstine, 2002). Similarly, it might be expected that DMS emission from leaves could help to sustain populations able to degrade this substrate. Such phyllosphere populations would probably affect the net flux of DMS and other volatile sulphur compounds emitted from plants. Whatever the function is of volatile sulphur release by plants, organisms degrading these compounds have the potential to affect the functioning of the biological systems that might rely on volatile compounds. Emission of volatile sulphur has been suggested as a route for the removal of excess sulphur (see the review by Rennenberg, 1984) or toxic HS- ions (Saini et al., 1995). A recent report suggests a role for H$_2$S emission as a plant defence signal in the context of sulphur-induced resistance of crops (Papenbrock et al., 2007). As a major volatile sulphur species emitted by plants, DMS may have a role that has yet to be determined.

There is also potential for interactions between plants and C$_1$-sulphur compound-degrading micro-organisms below-ground. The activity of soil microbial populations involved in the cycling of organic sulphur compounds is of particular importance for contributing to soil fertility, as the preferred sulphur source of plants is sulphate, but the majority of sulphur in soils is bound in organic form (Kertesz and Mirleau, 2004). Recent improvements with respect to anthropogenic emissions of sulphur from fossil fuel combustion have led to a reduction in man-made sulphate aerosols in the atmosphere and to a concomitant decrease in the rate of deposition of atmospheric sulphur (Irwin et al., 2002). In some areas, the decrease in atmospheric S deposition is leading to increasing incidences of sulphur deficiency for a range of agricultural crops, such as oilseed rape (Schlug et al., 1995). Evidence for a decline of ‘natural’ sulphur fertilization of soils derived from atmospheric sulphur due to fossil fuel combustion is provided by changes in the sulphur isotope ratio in wheat straw (Zhao et al., 2003). Consideration of future SO$_2$ emission rates (McGrath and Zhao, 1995) or future climate scenarios indicates that the potential for sulphur starvation in crops is likely to increase (Hartmann et al., 2008) with important consequences for agricultural productivity. Previous research has demonstrated that bacterial organo-sulphur compound-degrading populations in the rhizosphere play an important role in regenerating sulphate for uptake by crop plants, for instance, but work has so far focused on the utilization of alkane- and arylsulphonates and -sulphates as sulphur sources for bacteria (Kertesz and Mirleau, 2004; Schmalenberger et al., 2008, 2009). Further work is needed to appreciate fully the role of microbial populations degrading C$_1$-sulphur compounds such as DMSO, DMSO$_2$, and MSA, and the utilization of these compounds as both sulphur and carbon sources in the rhizosphere needs to be investigated. The potential importance of DMSO$_2$ and DMSO-degrading methylo trophs in the rhizosphere of plants has been demonstrated by the work of Borodina et al. (2000, 2002).

**Outlook**

DMS-degrading micro-organisms are widely distributed in the environment, but there is still a lack of insight into their
phylogenetic and functional diversity. The development and application of functional gene probes and stable isotope probing experiments will allow patterns in the distribution of DMS-degrading micro-organisms in nature to be deciphered. Functional genetic markers based on key enzymes of DMS metabolism and that of related compounds will also allow the role of DMS-degrading organisms in controlling fluxes of volatile sulphur to the atmosphere to be investigated in more detail and will help to assess their contribution to the metabolism of organically bound sulphur and of returning inorganic sulphur back to the environment. Clearly, the emission of DMS from the marine environment is controlled significantly by the activity of micro-organisms. Microbial DMS metabolism affects the flux of DMS to the atmosphere and thus the composition of the atmosphere and global climate. Therefore, the activity of marine microbial DMS-degrading micro-organisms is ultimately an important factor that influences the amount of sulphur transported to the continents where it affects the levels of sulphur in soils. Establishing the phylogenetic affiliation of DMS-degrading organisms in the environment and the identification of the pathways used by microbial populations to remove DMS from the water column will help to identify the environmental regulation of marine microbial DMS oxidation. This will contribute to gaining a better understanding of the complex microbial processes involved in controlling the flux of sulphur from the oceans into the atmosphere and should be useful in improving the prospects of modelling marine DMS emissions under future climatic scenarios.

Acknowledgements

We are grateful for funding provided by the Natural Environment Research Council provided through a studentship to RB and fellowships for HS (NE/B501404/1 and NE/E013333/1) and invaluable guidance, support and mentorship provided by Colin Murrell and Don Kelly.

References


Hyphomicrobium sulfonivorans


De Zwart JMM, Nelisse PN, Kuenen JG. 1996. Isolation and characterization of Methylophaga sulfidovorans sp. nov.: an obligately methylotrophic, aerobic, dimethylsulphoxide oxidizing bacterium from a microbial mat. FEMS Microbiology Ecology 20, 261–270.


Molecular analysis of dimethyl sulphide dehydrogenase from tomato products.


Todd JD, Curson ARJ, Dupont CL, Nicholson P, Johnston AWB. 2009. The dddP gene, encoding a novel enzyme that converts dimethylsulfoniopropionate into dimethyl sulfide, is widespread in ocean metagenomes and marine bacteria and also occurs in some Ascomycete fungi. Environmental Microbiology 11, 1376–1385.


