Journal of Experimental Botany, Vol. 61, No. 2, pp. 315–334, 2010
doi:10.1093/jxb/erp355 Advance Access publication 10 December, 2009

Journal of Experimental Botany
www.jxb.oxfordjournals.org

DARWIN REVIEW

Microbial degradation of dimethylsulphide and related C_1-sulphur compounds: organisms and pathways controlling fluxes of sulphur in the biosphere

Hendrik Schäfer[1,*], Natalia Myronova[1] and Rich Boden[2]

[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

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

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) dimethylsulphoniopropionate (DMSP), dimethylsulphoxide (DMSO), dimethylsulphone ($DMSO_2$), 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 $DMSO_2$ 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),

© The Author [2009]. Published by Oxford University Press [on behalf of the Society for Experimental Biology]. All rights reserved.
For Permissions, please e-mail: journals.permissions@oxfordjournals.org

Table 1. DMS and related organic sulphur compounds

Compound	Formula
Dimethylsulphide (DMS)	$(CH_3)_2$-S
Dimethylsulphonio-propionic acid (DMSP)	$(CH_3)_2$-S-CH_2-CH_2-COOH
Dimethylsulphoxide (DMSO)	$(CH_3)_2$-SO
Dimethylsulphone ($DMSO_2$)	$(CH_3)_2$-SO_2
Methanethiol (MT)	CH_3-SH
Dimethyldisulphide (DMDS)	CH_3-S-S-CH_3
Methanesulphonic acid (MSA)	CH_3-SO_3H

wines (Segurel *et al.*, 2004), orange and grapefruit juice (Shaw *et al.*, 1980), and is also found in roast coffee (Rhoades, 2002) and processed milk (Keenan and Lindsay, 1968). DMS can be part of the essential aroma profile but also be of concern as it can contribute to off-notes.

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 $DMSO_2$ are found in a wide range of foods including milk (Pearson *et al.*, 1981). Humans excrete 4–11 mg of $DMSO_2$ per day via urine. Marketed as methylsulphonylmethane, it is also a constituent of some dietary supplements (see Parcell, 2002, for a review).

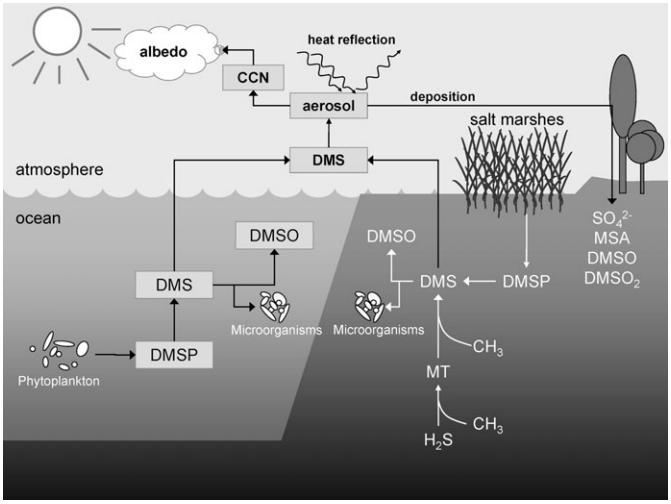

Fig. 1. Simplified scheme of the major pathways of DMS production and transformation in the marine environment. DMS emission into the atmosphere is a source of heat-reflecting aerosols that can serve as cloud condensation nuclei and thereby affect the radiative balance of the Earth, thus linking DMS 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.

Environmental significance of DMS and related compounds

The roles of C_1-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 corresponds to 20 million tons of sulfur which translates to emission of more than 50 kg of sulphur km^{-2} of ocean surface on average.

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 $DMSO_2$ 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 $DMSO_2$ (see Kertesz, 2000, for

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

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). Dimethylsulphoniopropionate (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 *Emilinia 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 DMSP, 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), DMSP 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

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

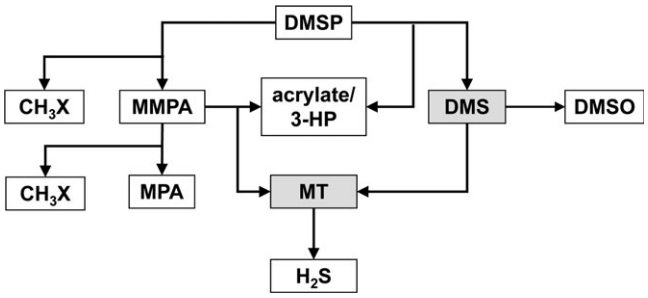

Fig. 2. Major pathways of dimethylsulphoniopropionate (DMSP) degradation. DMSP can be demethylated to methylmercaptopropionic acid (MMPA), which can be either demethylated to mercaptopropionic acid (MPA) or demethiolated to acrylate. The pathway leading to DMS from DMSP is also known as the 'cleavage' 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 is oxidized to DMSO, for instance by DMS dehydrogenase. Refer to text for references.

(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.*, 1997).

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, 1978*c*), 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 Bremner, 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 Bremner, 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 SO_2 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 Papvizas, 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 (Gamliel and Stapleton, 1993) with an additional contribution by less toxic volatile sulphur species such as DMDS (Bending and Lincoln, 1999). A combination of 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

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

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 H_2S, DMS, MT, COS, and CS_2, with H_2S 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 pCO_2 (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 (Glindemann *et al.*, 2006). Industrial operations providing composts for mushroom production (Derikx *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 H_2S, 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

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

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 and/or H_2S as intermediates, while other pathways do not give rise to volatile sulphur compounds. The scheme in Fig. 4 provides an overview of the conversions of DMS and related C_1-sulphur compounds that occur in a wide range of different organisms. Details of specific biochemical conversions of DMS and the micro-organisms that carry them out are presented below

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, 1993*b*). Formaldehyde is either directly assimilated into biomass or further oxidized via formate to CO_2 in order to provide reducing power. Assimilation of the formaldehyde produced during DMS and MT degradation in methylotrophic 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 CO_2, 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 CO_2 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 co-factors 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, 1993*b*). 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, 1993*a*, *b*). Further oxidation of the remaining methanethiol appeared to follow the same scheme as in the DMS monooxygenase pathway described above.

$DMSO_2$ 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

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

Table 2. Bacterial isolates capable of growth on DMS as a sole source of carbon and energy

Species	Strain	$[DMS]_{MAX}$	Isolated from	Isolation substrate (concentration)	Reference
Klebsiella pneumoniae[a]	ATCC 9621	ND	Unknown[b]	Unknown	Rammler and Zafferoni, 1967
Thiobacillus sp.	MS1	2.4 mM	*Pinus* sp. bark biofilter from a cellulose mill	DMS (1.6 mM)	Sivelä and Sundman, 1975
Hyphomicrobium sp.	S	ND	Soil (Wageningen, Netherlands)	DMSO (12.8 mM)	De Bont *et al.*, 1981
Thiobacillus thioparus	Tk-m	2 mM	Activated sludge	Thiometon (6 mM)	Kanagawa *et al.*, 1982; Kanagawa and Kelly, 1986
Hyphomicrobium sp.	EG	0.1 mM	Papermill biofilter	DMSO (10 mM)	Suylen and Kuenen, 1986
Thiobacillus sp.	E1	2 mM	Commercial peat	DMS (2 mM)	Smith, 1987
Thiobacillus sp.	E3	2 mM	Garden compost	DMS (2 mM)	Smith, 1987
Thiobacillus sp.	E4	2 mM	Cattle manure	DMS (2 mM)	Smith, 1987
Thiobacillus sp.	E5	2 mM	Marine mud (Plymouth, UK)	DMS (2 mM)	Smith, 1987
Thiobacillus sp.	E7	2 mM	*Sphagnum* sp. moss from a deodorization unit	DMDS (2 mM)	Smith, 1987
Thiobacillus thioparus	E6	2 mM	Pond water (Coventry, UK)	DMDS (2 mM)	Smith and Kelly, 1988
Hyphomicrobium sp.	I55	ND	Peat biofilter	DMS (1 mM)	Zhang *et al.*, 1991*a*
Thiobacillus thioparus	DW44	ND	Peat biofilter	Thiosulphate (20 mM)	Cho *et al.*, 1991
Thiobacillus sp.	K4	ND	Biofilter	CS_2	Plas *et al.*, 1991
Thiobacillus sp.	T5	1.3 mM	Marine microbial mat (Texel, Netherlands)	Thiosulphate (10 mM)	Visscher *et al.*, 1991
Thiobacillus sp.	ANS-1	ND	Tidal sediment (Georgia, USA)	DMS (0.5 mM)	Visscher and Taylor, 1993*b*
Hyphomicrobium sp.	VS	1 mM	Activated sludge	DMS (15 μM)	Pol *et al.*, 1994
Desulfotomaculum sp.	TDS2	ND	Thermophilic fermenter sludge	DMS (5 mM) and 10 mM sulphate	Tanimoto and Bak, 1994
Desulfotomaculum sp.	SDN4	ND	Thermophilic fermenter sludge	DMS (5 mM) and 5 mM nitrate	Tanimoto and Bak, 1994
Methylophaga sulfidovorans	RB-1	2.4 mM	Marine microbial mat (Texel, Netherlands)	DMS (1.5 mM)	de Zwart *et al.*, 1996
Hyphomicrobium sp.	MS3	ND	Garden soil (Ghent, Belgium)	DMS/DMDS (1.4/1.1 mM)	Smet *et al.*, 1996
Xanthobacter tagetidis	TagT2C	2.5 mM	*Tagetes patula* rhizosphere	T2C(2.5 mM)	Padden *et al.*, 1997
Pseudonocardia asaccharolytica	580	ND	Animal rendering plant biofilter	DMDS (1 mM)	Reichert *et al.*, 1998
Pseudonocardia sulfidoxydans	592	ND	Animal rendering plant biofilter	DMS (0.5 mM)	Reichert *et al.*, 1998
Starkeya novella[c]	SRM	ND	Sewage (Kwangju, South Korea)	Thiosulphate (63 mM)	Cha *et al.*, 1999
Thiocapsa roseopersicina	M11	1 mM	Marine microbial mat (Mellum, Germany)	Sulphide (1.6 mM)	Jonkers *et al.*, 1999
Methylobacterium podarium	FM1	ND	*Homo sapiens* foot	MMA (20 mM)	Vohra, 2000
Hyphomicrobium sulfonivorans	S1	ND	Garden soil (Warwickshire, UK)	$DMSO_2$ (10 mM)	Borodina *et al.*, 2002
Arthrobacter sulfonivorans	ALL/A	ND	*Allium aflatunense* rhizosphere	$DMSO_2$ (10 mM)	Borodina *et al.*, 2002
Arthrobacter sulfonivorans	ALL/B	ND	*Allium aflatunense* rhizosphere	$DMSO_2$ (10 mM)	Borodina *et al.*, 2002
Arthrobacter methylotrophus	TGA	ND	*Tagetes minuta* rhizosphere	$DMSO_2$ (10 mM)	Borodina *et al.*, 2002
Methylobacterium podarium	FM4	1 mM	*Homo sapiens* foot	MMA (20 mM)	Anesti *et al.*, 2004
Hyphomicrobium sulfonivorans	CT	ND	*Homo sapiens* teeth	DMS (1 mM)	Anesti *et al.*, 2005
Hyphomicrobium sulfonivorans	DTg	ND	*Homo sapiens* tongue	DMS (1 mM)	Anesti *et al.*, 2005
Methylobacterium thiocyanatum	MM4	ND	*Homo sapiens* tongue	MMA (20 mM)	Anesti *et al.*, 2005
Methylobacterium extorquens	MM9	ND	*Homo sapiens* tongue	Methionine (5 mM)	Anesti *et al.*, 2005
Methylobacterium sp.	MM10	ND	*Homo sapiens* tongue	Cysteine (5 mM)	Anesti *et al.*, 2005
Micrococcus luteus	MM7	ND	*Homo sapiens* teeth	MMA (20 mM)	Anesti *et al.*, 2005
Bacillus licheniformis	3S(b)	ND	*Homo sapiens* gingivae	DMS (1 mM)	Anesti *et al.*, 2005
Bacillus licheniformis	2Tgb	ND	*Homo sapiens* tongue	DMS (1 mM)	Anesti *et al.*, 2005
Brevibacterium casei	3Tg	ND	*Homo sapiens* tongue	DMS (1 mM)	Anesti *et al.*, 2005
Brevibacterium casei	3S(a)	ND	*Homo sapiens* gingivae	DMS (1 mM)	Anesti *et al.*, 2005
Mycobacterium fluoranthenivorans	DSQ3	ND	River sediment (London, UK)	DMA (10 mM)	Boden, 2005; Boden *et al.*, 2008

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

Table 2. *Continued*

Species	Strain	$[DMS]_{MAX}$	Isolated from	Isolation substrate (concentration)	Reference
Methylophaga sp.	DMS001	ND	*Emiliania huxleyi* culture	DMS (50 μM)	Schäfer, 2007
Methylophaga sp.	DMS002	ND	*Emiliania huxleyi* culture	DMS (50 μM)	Schäfer, 2007
Methylophaga sp.	DMS003	ND	*Emiliania huxleyi* culture	DMS (50 μM)	Schäfer, 2007
Methylophaga sp.	DMS004	ND	*Emiliania huxleyi* culture	DMS (50 μM)	Schäfer, 2007
Methylophaga sp.	DMS007	ND	*Emiliania huxleyi* culture	DMS (50 μM)	Schäfer, 2007
Methylophaga sp.	DMS009	ND	*Emiliania huxleyi* culture	DMS (50 μM)	Schäfer, 2007
Methylophaga thiooxidans[d]	DMS010	ND	*Emiliania huxleyi* culture	DMS (50 μM)	Schäfer, 2007
Methylophaga sp.	DMS011	ND	*Emiliania huxleyi* culture	DMS (50 μM)	Schäfer, 2007
Methylophaga sp.	DMS021	ND	Rock pool water (Coral Beach, UK)	DMS (50 μM)	Schäfer, 2007
Methylophaga sp.	DMS026	ND	Sea water (English channel)	DMS (50 μM)	Schäfer, 2007
Methylophaga sp.	DMS039	ND	Sea water (Achmelvich, UK)	DMS (50 μM)	Schäfer, 2007
Methylophaga sp.	DMS040	ND	Sea water (Achmelvich, UK)	DMS (50 μM)	Schäfer, 2007
Methylophaga sp.	DMS043	ND	Sea water (Achmelvich, UK)	DMS (50 μM)	Schäfer, 2007
Methylophaga sp.	DMS044	ND	Sea water (Achmelvich, UK)	DMS (50 μM)	Schäfer, 2007
Methylophaga sp.	DMS048	ND	Rock pool water (Coral Beach, UK)	Formate (10 mM)	Schäfer, 2007
Methylophaga aminisulfidivorans[e]	MP*	ND	Sea water (Mokpo, South Korea)	Methanol (220 mM)	Kim *et al.*, 2007
Hyphomicrobium facile	–	ND	Marsh sediment (De Bruuk, Netherlands)	DMS (50 μM)	Haaijer *et al.*, 2008
Microbacterium sp.	NTUT26	ND	Wastewater sludge from a wood pulp factory (Taiwan)	DMS (1.6 mM)	Shu and Chen, 2009
Desulfosarcina sp.	SD1	ND	Mangrove sediment (Tanzania)	DMS (initially 20 μM, additions rising to 100 μM)	Lyimo *et al.*, 2009

[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

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

[a] 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.

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

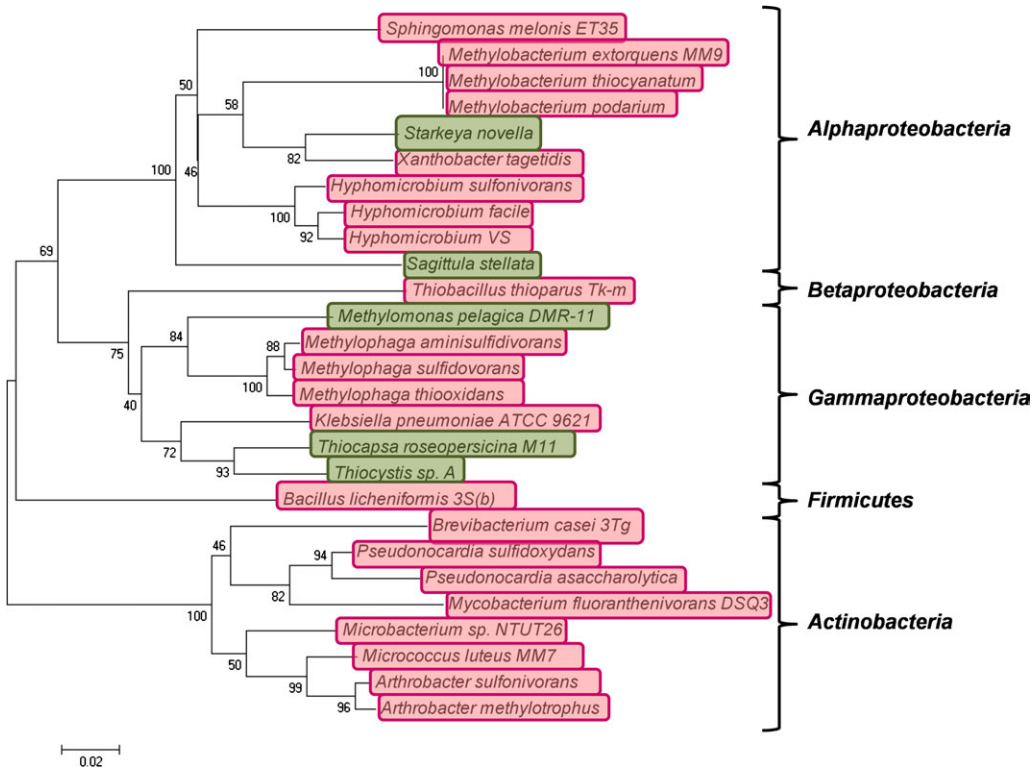

Fig. 3. Phylogenetic tree depicting the genetic diversity of bacterial isolates capable of assimilating carbon from DMS (overlaid in pink) or degrading DMS to DMSO (green). The tree is based on an alignment of small subunit ribosomal RNA gene sequences and was derived using the Neighbor–Joining option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

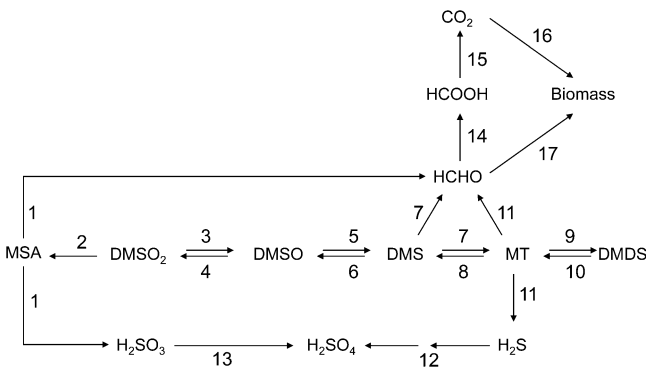

Fig. 4. Scheme showing the biochemical and chemical interconversions of C_1-sulphur compounds and key intermediates in carbon and sulphur metabolism that have been observed across a wide range of micro-organisms (refer to Table 1 for chemical formulae of the C_1-sulphur compounds). Either the enzymes/processes 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, $FMNH_2$-dependent $DMSO_2$ monooxygenase (Endoh *et al.*, 2005); 3, $DMSO_2$ 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.

was DMSO, which was reduced to DMS and thus fed into the DMS monooxygenase pathway. Subsequently, it was shown that $DMSO_2$ could also be degraded by some methylotrophs via DMS, as enzyme activities for $DMSO_2$ 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*a*; Tanimoto and Bak, 1994; Lomans *et al.*, 1999*b*; 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*b*; Kiene *et al.*, 1986; Kiene and Capone, 1988; Lomans *et al.*, 1999*a*), but the degradation of DMS has also been reported with nitrate as electron acceptor (Visscher and Taylor, 1993*a*; Tanimoto and Bak, 1994; Haaijer *et al.*, 2008). The characteristics of methanogenic Archaea growing on DMS and MT have been reviewed previously, with isolates belonging to the genera *Methanolobus*, *Methanomethylovorans*, *Methanosarcina*, and

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

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 *Desulfosarcina* 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.* (1991*b*) in *Pseudomonas acidovorans* DMR-11 (reclassified as *Delftia 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 DMR-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 *Sagittula 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 *Sagittula stellata* and *Delftia 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 comprizing 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 *ddh* operon containing the genes *ddhABCD*, which encode the A, B (containing putative [Fe-S] clusters) and C (containing a *b*-type haem) subunits, and *ddhD* is thought to encode a polypeptide that could be responsible for the maturation of the molypdopterin-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 *Methylomicrobium* (Fuse *et al.*, 1998; Sorokin *et al.*, 2000) and in *Methylomicrobium pelagicum* the product was identified as DMSO. The nitrifying bacteria *Nitrosomonas europaea* and *Nitrosococcus oceani* (Juliette *et al.*, 1993) also converted DMS to DMSO and some evidence suggests that ammonia monooxygenase (AMO) is the enzyme co-oxidizing DMS to DMSO in these bacteria. While the co-oxidation of MT by purified methane monooxygenase (MMO), 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, 1978*a*). 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 molybdopterin co-factor, an electron transfer protein DmsB (23.6 kDa), and a membrane anchor DmsC (22.7 kDa) (Sambasivarao *et al.*, 1990). Despite the

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

differences in enzyme structure, the catalytic subunits of *R. spharoides* 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 $DMSO_2$, 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 K_s 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, the oxic mixed surface layer of the oceans.

Assimilation of C_1 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 $DMSO_2$ as sulphur sources and, in both strains, the sequence of oxidation started with DMS oxidation to DMSO which was oxidized to $DMSO_2$ 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).

MSA catabolism

A different kind of methanesulphonate monooxygenase exists in methylotrophic bacteria such as *Methylosulfonomonas methylovora* 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 $\alpha 3/\beta 3$ structure. Further components were identified as a ferredoxin (32 kDa) and a reductase (38 kDa). The enzyme subunits are encoded by the genes *msmABCD* (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 *msmABCD* 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*, and *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 phylotype 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

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

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-Nkpwatt *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_2S 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 (Schnug *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 methylotrophs 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

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

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

Abanda-Nkpwatt D, Musch M, Tschiersch J, Boettner M, Schwab W. 2006. Molecular interaction between *Methylobacterium extorquens* and seedlings: growth promotion, methanol consumption, and localization of the methanol emission site. *Journal of Experimental Botany* **57,** 4025–4032.

Adams B, Smith AT, Bailey S, McEwan AG, Bray RC. 1999. Reactions of dimethylsulphoxide reductase from *Rhodobacter capsulatus* with dimethyl sulphide and with dimethyl sulphoxide: complexities revealed by conventional and stopped-flow spectrophotometry. *Biochemistry* **38,** 8501–8511.

Andreae MO. 1990. Ocean–atmosphere interactions in the global biogeochemical sulphur cycle. *Marine Chemistry* **30,** 1–29.

Anesti V, McDonald IR, Ramaswamy M, Wade WG, Kelly DP, Wood AP. 2005. Isolation and molecular detection of methylotrophic bacteria ocurring in the human mouth. *Environmental Microbiology* **7,** 1227–1238.

Anesti V, Vohra J, Goonetilleka S, McDonald IR, Sträubler B, Stackebrandt E, Kelly DP, Wood AP. 2004. Molecular detection and isolation of facultatively methylotrophic bacteria, including *Methylobacterium podarium* sp. nov., from the human foot microflora. *Environmental Microbiology* **6,** 820–830.

Anthony C. 1982. *The biochemistry of methylotrophs*. London: Academic Press.

Archer SD, Smith GC, Nightingale PD, Widdicombe CE, Tarran GA, Rees AP, Burkill PH. 2002. Dynamics of particulate dimethylsulphoniopropionate during a Lagrangian experiment in the northern North Sea. Deep sea research. Part II: *Topical Studies in Oceanography* **49,** 2979–2999.

Ayers GP, Cainey JM, Gillett RW, Ivey JP. 1997. Atmospheric sulphur and cloud condensation nuclei in marine air in the Southern Hemisphere. *Philosophical Transactions of the Royal Society B* **352,** 203–211.

Ayers GP, Ivey JP, Gillett RW. 1991. Coherence between seasonal cycles of dimethyl sulphide, methanesulphonate and sulphate in marine air. *Nature* **349,** 404–406.

Bak F, Finster K, Rothfuß F. 1992. Formation of dimethylsulfide and methanethiol from methoxylated aromatic compounds and inorganic sulfide by newly isolated anaerobic bacteria. *Archives of Microbiology* **157,** 529–534.

Banwart WL, Bremner JM. 1976. Volatilization of sulfur from unamended and sulfate-treated soils. *Soil Biology and Biochemistry* **8,** 19–22.

Barnes I, Hjorth J, Mihalopoulos. 2006. Dimethyl sulfide and dimethyl sulfoxide and their oxidation in the atmosphere. *Chemical Reviews* **106,** 940–975.

Bending GD, Lincoln SD. 1999. Characterization of volatile sulphur-containing compounds produced during decomposition of *Brassica juncea* tissues in soil. *Soil Biology and Biochemistry* **31,** 695–703.

Bending GD, Lincoln SD. 2000. Inhibition of soil nitrifying bacteria communities and their activities by glucosinolate hydrolysis products. *Soil Biology and Biochemistry* **32,** 1261–1269.

Bills DD, Keenan TW. 1968. Dimethyl sulfide and its precursor in sweet corn. *Journal of Agricultural and Food Chemistry* **16,** 643–645.

Bilous PT, Cole ST, Anderson WF, Weiner JH. 1988. Nucleotide sequence of the *dmsABC* operon encoding the anaerobic dimethylsulphoxide reductase of *Escherichia coli*. *Molecular Microbiology* **2,** 785–795.

Bopp L, Aumont O, Belviso S, Monfray P. 2003. Potential impact of climate change on marine dimethylsulfide emissions. *Tellus B* **55,** 11–22.

Boden R. 2005. Isolation and characterization of bacteria capable of growth on methylated amines as sole source of carbon, nitrogen and energy. BSc dissertation, King's College, London (UK).

Boden R, Thomas E, Savani P, Kelly DP, Wood AP. 2008. Novel methylotrophic bacteria isolated from the River Thames (London, UK). *Environmental Microbiology* **10,** 3225–3236.

Borodina E, Kelly DP, Rainey FA, Ward-Rainey NL, Wood AP. 2000. Dimethylsulfone as a growth substrate for novel methylotrophic

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

species of *Hyphomicrobium* and *Arthrobacter*. *Archives of Microbiology* **173,** 425–437.

Borodina E, Kelly DP, Schumann P, Rainey FA, Ward-Rainey NL, Wood AP. 2002. Enzymes of dimethylsulfone metabolism and the phylogenetic characterization of the facultative methylotrophs *Arthrobacter sulfonivorans* sp. nov., *Arthrobacter methylotrophus* sp. nov., and *Hyphomicrobium sulfonivorans* sp. nov. *Archives of Microbiology* **177,** 173–183.

Brimblecombe P, Shooter D. 1986. Photooxidation of dimethylsulfide in aqueous solution. *Marine Chemistry* **19,** 343–353.

Broadbent AD, Jones GB. 2004. DMS and DMSP in mucus ropes, coral mucus, surface films and sediment pore waters from coral reefs in the Great Barrier Reef. *Marine And Freshwater Research* **55,** 849–855.

Buttery RG, Guadagni DG, Ling LC, Seifert RM, Lipton W. 2002. Additional volatile components of cabbage, broccoli, and cauliflower. *Journal of Agricultural and Food Chemistry* **24,** 829–832.

Caron F, Kramer JR. 1994. Formation of volatile sulfides in freshwater environments. *The Science of the Total Environment* **153,** 177–194.

Catalan L, Lian V, Johnson A, Jia C, O'Connor B, Walton C. 2008. Emissions of reduced sulphur compounds from the surface of primary and secondary wastewater clarifiers at a Kraft Mill. *Environmental Monitoring and Assessment.* DOI 10.1007/s10661-008-0461-9.

Cha JM, Cha WS, Lee JH. 1999. Removal of organo-sulphur odour compounds by *Thiobacillus novellus* SRM, sulphur-oxidizing micro-organisms. *Process Biochemistry* **34,** 659–665.

Challenger F, Simpson MI. 1948. Studies on biological methylation. Part XII. A precursor of the dimethyl sulphide evolved by *Polysiphonia fastigiata*. dimethyl-2-carboxyethylsulphonium hydroxide and its salts. *Journal of the Chemical Society* **3,** 1591–1597.

Charlson RJ, Lovelock JE, Andreae MO, Warren SG. 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature* **326,** 655–661.

Cho KS, Hirai M, Shoda M. 1991. Degradation characteristics of hydrogen-sulphide, methanethiol, dimethyl sulfide and dimethyl disulfide by *Thiobacillus thioparus* DW44 isolated from peat biofilter. *Journal of Fermentation and Bioengineering* **71,** 384–389.

Colby J, Stirling DI, Dalton H. 1977. The soluble methane mono-oxygenase of *Methylococcus capsulatus* (Bath): Its ability to oxygenate n-alkanes, n-alkenes, ethers and alicyclic, aromatic and heterocyclic compounds. *Biochemical Journal* **165,** 395–402.

Cooper DJ, Cooper WJ, de Mello WZ, Saltzman ES, Zika RG. 1989. Variability in biogenic sulphur emissions from Florida wetlands. In: Saltzman ES, Cooper WJ, eds. *Biogenic sulphur in the environment*. ACS, 31–43.

Curson ARJ, Rogers R, Todd JD, Brearley CA, Johnston AWB. 2008. Molecular genetic analysis of a dimethylsulfoniopropionate lyase that liberates the climate-changing gas dimethylsulfide in several marine alpha-proteobacteria and *Rhodobacter sphaeroides*. *Environmental Microbiology* **10,** 757–767.

De Bont JAM, van Dijken JP, Harder W. 1981. Dimethyl sulphoxide and dimethyl sulphide as a carbon, sulphur and energy source for growth of *Hyphomicrobium* S. *Journal of General Microbiology* **127,** 315–323.

de la Fuente E, Sanz ML, Martinez-Castro I, Sanz J, Ruiz-Matute AI. 2007. Volatile and carbohydrate composition of rare unifloral honeys from Spain. *Food Chemistry* **105,** 84–93.

De Marco P, Moradas-Ferreira P, Higgins TP, McDonald I, Kenna EM, Murrell JC. 1999. Molecular analysis of a novel methanesulfonic acid monooxygenase from the methylotroph *Methylosulfonomonas methylovora*. *Journal of Bacteriology* **181,** 2244–2251.

Derikx PJL, Op Den Camp HJM, Van Der Drift C, Van Griensven LJLD, Vogels GD. 1990. Odorous sulphur compounds emitted during production of compost used as a substrate in mushroom cultivation. *Applied and Environmental Microbiology* **56,** 176–180.

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

Drotar A, Burton Jr GA, Tavernier JE, Fall R. 1987. Widespread occurrence of bacterial thiol methyltransferases and the biogenic emission of methylated sulphur gases. *Applied and Environmental Microbiology* **53,** 1626–1631.

Eichhorn E, van der Ploeg JR, Leizinger T. 1999. Characterization of a two-component alkanesulfonate monooxygenase from *Escherichia coli*. *Journal of Biological Chemistry* **274,** 26639–26646.

Endoh T, Habe H, Yoshida T, Nojiri H, Omori T. 2003. A CysB-regulated and σ54-dependent regulator, SfnR, is essential for dimethyl sulphone metabolism of *Pseudomonas putida* DS1. *Microbiology* **149,** 991–1000.

Endoh T, Habe H, Nojiri H, Yamane H, Omori T. 2005. The σ^{54}-dependent transcriptional activator SfnR regulates the expression of the *Pseudomonas putida* sfnFG operon responsible for dimethyl sulphone utilization. *Molecular Microbiology* **55,** 897–911.

Fall R, Albritton DL, Fehsenfeld FC, Kuster WC, Goldan PD. 1988. Laboratory studies of some environmental variables controlling sulfur emissions from plants. *Journal of Atmospheric Chemistry* **6,** 341–362.

Finster K, Tanimoto Y, Bak F. 1992. Fermentation of methanethiol and dimethylsulphide by a newly isolated methanogenic bacterium. *Archives of Microbiology* **157,** 425–430.

Fritz M, Bachofen R. 2000. Volatile organic sulfur compounds in a meromictic alpine lake. *Acta Hydrochimica Hydrobiologica* **28,** 185–192.

Fuse H, Ohta M, Takimura O, Murakami K, Inoue H, Yamaoka Y, Oclarit JM, Omori T. 1998. Oxidation of trichloroethylene and dimethyl sulfide by a marine *Methylomicrobium* strain containing soluble methane monooxygenase. *Bioscience Biotechnology and Biochemistry* **62,** 1925–1931.

Fuse H, Takimura O, Murakami K, Yamoaka Y, Omori T. 2000. Utilization of dimethyl sulfide as a sulfur source with the aid of light by *Marinobacterium* sp. strain DMS-S1. *Applied and Environmental Microbiology* **66,** 5527–5532.

Galbally IE, Kirstine W. 2002. The production of methanol by flowering plants and the global cycle of methanol. *Journal of Atmospheric Chemistry* **43,** 195–229.

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

Gamliel A, Stapleton JJ. 1993. Characterization of antifungal volatile compounds evolved from solarized soil amended with cabbage residues. *Phytopathology* **83,** 899–905.

Geng CM, Mu YJ. 2006. Carbonyl sulfide and dimethyl sulfide exchange between trees and the atmosphere. *Atmospheric Environment* **40,** 1373–1383.

Ginzburg B, Chalifa I, Gun J, Dor I, Hadas O, Lev O. 1998. DMS formation by dimethylsulfoniopropionate route in freshwater. *Environmental Science and Technology* **32,** 2130–2136.

Glindemann D, Novak J, Witherspoon J. 2006. Dimethyl sulfoxide (DMSO) waste residues and municipal waste water odor by dimethyl sulfide (DMS): the north-east WPCP plant of Philadelphia. *Environmental Science and Technology* **40,** 202–207.

González JM, Kiene RP, Moran MA. 1999. Transformation of sulfur compounds by an abundant lineage of marine bacteria in the alpha-subclass of the class Proteobacteria. *Applied and Environmental Microbiology* **65,** 3810–3819.

González JM, Mayer F, Moran MA, Hodson RE, Whitman WB. 1997. *Sagittula stellata* gen. nov., sp. nov., a lignin-transforming bacterium from a coastal environment. *International Journal of Systematic Bacteriology* **47,** 773–780.

Gould WD, Kanagawa T. 1992. Purification and properties of methyl mercaptan oxidase from *Thiobacillus thioparus* TK-m. *Journal of General Microbiology* **138,** 217–221.

Haaijer SCM, Harhangi HR, Meijerink BB, Strous M, Pol A, Smolders AJP, Verwegen K, Jetten MSM, den Camp H. 2008. Bacteria associated with iron seeps in a sulfur-rich, neutral pH, freshwater ecosystem. *ISME Journal* **2,** 1231–1242.

Hanlon SP, Holt RA, Moore GR, McEwan AG. 1994. Isolation and characterization of a strain of *Rhodobacter sulfidophilus*: a bacterium which grows autotrophically with dimethylsulfide as electron-donor. *Microbiology-UK* **140,** 1953–1958.

Hanlon SP, Toh TH, Solomon PS, Holt RA, McEwan AG. 1996. Dimethylsulphide:acceptor oxidoreductase from *Rhodobacter sulfidophilus*: the purified enzyme contains *b*-type haem and a pterin molybdenum cofactor. *European Journal of Biochemistry* **239,** 391–396.

Hartmann K, Lilienthal H, Schnug E. 2008. Risk-mapping of potential sulphur deficiency in agriculture under actual and future climate scenarios in Germany. *Aspects of Applied Biology* **88,** 113–121.

Harvey GR, Lang RF. 1986. Dimethylsulfoxide and dimethylsulfone in the marine atmosphere. *Geophysical Research Letters* **13,** 49–51.

Hatakeyama S, Okuda M, Akimoto H. 1982. Formation of sulfur dioxide and methanesulfonic acid in the photooxidation of dimethyl sulfide in the air. *Geophysical Research Letters* **9,** 583–586.

Hatton AD, Darroch L, Malin G. 2004. The role of dimethylsulphoxide in the marine biogeochemical cycle of dimethylsulphide. In: Gibson RN, Atkinson RJA, Gordon JDM, eds. *Oceanography and marine biology: an annual review*. Boca Raton: CRC Press, 29–55.

Hill RW, Dacey JWH, Krupp DA. 1995. Dimethylsulphoniopropionate in reef corals. *Bulletin of Marine Science* **57,** 489–494.

Holmes AJ, Costello A, Lidstrom ME, Murrell JC. 1995. Evidence that particulate methane monooxygenase and ammonia monooxygenase may be evolutionarily related. *FEMS Microbiology Letters* **132,** 203–208.

Horinouchi M, Kasuga K, Nojiri H, Yamane H, Omori T. 1997. Cloning and characterization of genes encoding an enzyme which oxidizes dimethyl sulfide in *Acinetobacter* sp. strain 20B. *FEMS Microbiology Letters* **155,** 99–105.

Howard EC, Henriksen JR, Buchan A, *et al*. 2006. Bacterial taxa that limit sulfur flux from the ocean. *Science* **314,** 649–652.

Irwin JG, Campbell G, Vincent K. 2002. Trends in sulphate and nitrate wet deposition over the United Kingdom: 1986–1999. *Atmospheric Environment* **36,** 2867–2879.

Jamshad M, De Marco P, Pacheco CC, Hanczar T, Murrell JC. 2006. Identification, mutagenesis, and transcriptional analysis of the methanesulfonate transport operon of *Methylosulfonomonas methylovora*. *Applied and Environmental Microbiology* **72,** 276–283.

Johnston AWB, Todd JD, Sun L, Nikolaidou-Katsaridou MN, Curson ARJ, Rogers R. 2008. Molecular diversity of bacterial production of the climate-changing gas, dimethyl sulphide, a molecule that impinges on local and global symbioses. *Journal of Experimental Botany* **59,** 1059–1067.

Jonkers HM, Koopmans GF, van Gemerden H. 1998. Dynamics of dimethyl sulfide in a marine microbial mat. *Microbial Ecology* **36,** 93–100.

Jonkers HM, van der Maarel MJEC, van Gemerden H, Hansen T. 1996. Dimethylsulfoxide reduction by marine sulfate-reducing bacteria. *FEMS Microbiology Letters* **136,** 283–287.

Juliette LY, Hyman MR, Arp DJ. 1993. Inhibition of ammonia oxidation in *Nitrosomonas europaea* by sulfur compounds: thioethers are oxidized to sulfoxides by ammonia monooxygenase. *Applied and Environmental Microbiology* **59,** 3718–3727.

Kadota H, Ishida Y. 1972. Production of volatile sulfur compounds by micro-organisms. *Annual Review of Microbiology* **26,** 127–138.

Kalinová B, Podskalská H, Růžička J, Hoskovec M. 2009. Irresistible bouquet of death: how are burying beetles (Coleoptera: Silphidae: *Nicrophorus*) attracted by carcasses. *Naturwissenschaften* doi 10.1007/s00114-009-0545-6.

Kanagawa T, Kelly DP. 1986. Breakdown of dimethyl sulfide by mixed cultures and by *Thiobacillus thioparus*. *FEMS Microbiology Letters* **34,** 13–19.

Kanagawa T, Dazai M, Fukuoka S. 1982. Degradation of *O*,*O*-dimethyl phosphorodithioate by *Thiobacillus thioparus* TK-1 and *Pseudomonas* AK-2. *Agricultural Biology and Chemistry* **46,** 2571–2578.

Keenan TW, Lindsay RC. 1968. Evidence for a dimethyl sulfide precursor in milk. *Journal of Dairy Science* **51,** 112–113.

Kelly DP, Baker SC. 1990. The organosulfur cycle: aerobic and anaerobic processes leading to turnover of C_1-sulfur compounds. *FEMS Microbiology Reviews* **87,** 241–246.

Kelly DP, Murrell JC. 1999. Microbial metabolism of methanesulfonic acid. *Archives of Microbiology* **172,** 341–348.

Kertesz MA. 2000. Riding the sulfur cycle: metabolism of sulfonates and sulfate esters in Gram-negative bacteria. *FEMS Microbiology Reviews* **24,** 135–175.

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

Kertesz MA, Mirleau P. 2004. The role of soil microbes in plant sulphur nutrition. *Journal of Experimental Botany* **55,** 1939–1945.

Kertesz MA, Schmidt-Larbig K, Wüest T. 1999. A novel reduced flavin mononucleotide-dependent methanesulphonatase encoded by the sulfur-regulated *msu* operon of *Pseudomonas aeruginosa*. *Journal of Bacteriology* **181,** 1464–1473.

Kettle AJ, Andreae MO, Amouroux D, *et al*. 1999. A global database of sea surface dimethylsulfide (DMS) measurements and a procedure to predict sea surface DMS as a function of latitude, longitude, and month. *Global Biogeochemical Cycles* **13,** 399–444.

Kiene RP. 1988. Dimethyl sulphide metabolism in salt marsh sediments. *FEMS Microbiology Ecology* **53,** 71–78.

Kiene RP. 1990. Dimethyl sulfide production from dimethylsulfoniopropionate in coastal seawater samples and bacterial cultures. *Applied and Environmental Microbiology* **56,** 3292–3297.

Kiene RP, Bates TS. 1990. Biological removal of dimethyl sulfide from sea-water. *Nature* **345,** 702–705.

Kiene RP, Capone DG. 1988. Microbial transformations of methylated sulfur compounds in anoxic salt marsh sediments. *Microbial Ecology* **15,** 275–291.

Kiene RP, Gerard G. 1994. Determination of trace levels of dimethylsulfoxide (DMSO) in seawater and rainwater. *Marine Chemistry* **47,** 1–12.

Kiene RP, Hines ME. 1995. Microbial formation of dimethyl sulfide in anoxic *Sphagnum* peat. *Applied and Environmental Microbiology* **61,** 2720–2726.

Kiene RP, Linn LJ, Bruton JA. 2000. New and important roles for DMSP in marine microbial communities. *Journal of Sea Research* **43,** 209–224.

Kiene RP, Oremland RS, Catena A, Miller LG, Capone DG. 1986. Metabolism of reduced methylated sulfur compounds in anaerobic sediments an by a pure culture of an estuarine methanogen. *Applied and Environmental Microbiology* **52,** 1037–1045.

Kim HG, Doronina NV, Trotsenko YA, Kim SW. 2007. *Methylophaga aminisulfidivorans* sp nov., a restricted facultatively methylotrophic marine bacterium. *International Journal of Systematic and Evolutionary Microbiology* **57,** 2096–2101.

Kim KH, Choi YJ, Jeon EC, Sunwoo Y. 2005. Characterization of malodorous sulphur compounds in landfill gas. *Atmospheric Environment* **39,** 1103–1112.

Kim KY, Ko HJ, Kim HT, Kim YS, Roh YM, Lee CM, Kim HS, Kim CN. 2007. Sulfuric odorous compounds emitted from pig-feeding operations. *Atmospheric Environment* **41,** 4811–4818.

Kim S-J, Shin H-J, Kim Y-C, Lee D-S, Yang J-W. 2000. Isolation and purification of methyl mercaptan oxidase from *Rhodococcus rhodochrous* for mercaptan detection. *Biotechnology Bioprocess Engineering* **5,** 465–468.

Kinsela AS, Reynolds JK, Melville MD. 2007. Agricultural acid sulfate soils: a potential source of volatile sulfur compounds? *Environmental Chemistry* **4,** 18–25.

Kirst GO, Thiel C, Wolff H, Nothnagel J, Wanzek M, Ulmke R. 1991. Dimethylsulfoniopropionate (DMS) in ice-algae and its possible role. *Marine Chemistry* **35,** 381–388.

Knief C, Frances L, Cantet F, Vorholt JA. 2008. Cultivation-independent characterization of *Methylobacterium* populations in the plant phyllosphere by automated ribosomal intergenic spacer analysis. *Applied and Environmental Microbiology* **74,** 2218–2228.

Kubec R, Drhova V, Velisek J. 1998. Thermal degradation of *S*-methylcysteine and its sulfoxide important flavor precursors of *Brassica* and *Allium* vegetables. *Journal of Agricultural and Food Chemistry* **46,** 4334–4340.

Leake CD. 1967. Introductory remarks. *Annals of the New York Academy of Science* **141,** 1–3.

Lee H-H, Kim S-J, Shin H-J, Park J-Y, Yang J-W. 2002. Purification and characterisation of methyl mercaptan oxidase from *Thiobacillus thioparus* for mercaptan detection. *Biotechnology Bioprocess Engineering* **7,** 375–379.

Lewis JA, Papvizas GC. 1970. Evolution of volatile sulphur-containing compounds from decomposition of crucifers in soil. *Soil Biology and Biochemistry* **2,** 239–246.

Liss PS, Malin G, Turner S, Holligan PM. 1994. Dimethyl sulfide and *Phaeocystis*: a review. *Journal of Marine Systems* **5,** 41–53.

Liss PS, Merlivat L. 1986. Air–sea gas exchange rates: introduction and synthesis. In: Buat-Menard P, ed. *The role of air-sea exchange in geochemical cycling*. Dordrecht: D Reidel, 113–127.

Lomans BP, Leijdekkers P, Wesselink J-J, Bakkes P, Pol A, van der Drift C, Op den Camp HJ. 2001. Obligate sulfide-dependent degradation of methoxylated aromatic compounds and formation of methanethiol and dimethyl sulfide by a freshwater sediment isolate, *Parasporobacterium paucivorans* gen. nov., sp. nov. *Applied and Environmental Microbiology* **67,** 4017–4023.

Lomans BP, Maas R, Luderer R, Op den Camp HJ, Pol A, van der Drift C, Vogels GD. 1999*b*. Isolation and characterization of *Methanomethylovorans hollandica* gen. nov., sp. nov., isolated from freshwater sediment, a methylotrophic methanogen able to grow on dimethyl sulfide and methanethiol. *Applied and Environmental Microbiology* **65,** 3641–3650.

Lomans BP, Op den Camp HJ, Pol A, van der Drift C, Vogels GD. 1999*a*. Role of methanogens and other bacteria in degradation of dimethyl sulfide and methanethiol in anoxic freshwater sediments. *Applied and Environmental Microbiology* **65,** 2116–2121.

Lomans BP, Smolders AJP, Intven LM, Pol A, Op Den Camp HJM, Van Der Drift C. 1997. Formation of dimethyl sulfide and methanethiol in anoxic freshwater sediments. *Applied and Environmental Microbiology* **67,** 4741–4747.

Lomans BP, van der Drift C, Pol A, Op den Camp HJM. 2002. Microbial cycling of volatile organosulfur compounds. *Cellular and Molecular Life Sciences* **59,** 575–588.

Lovelock JE, Maggs RJ, Rasmussen RA. 1972. Atmospheric dimethyl sulphide and the natural sulphur cycle. *Nature* **237,** 452–453.

Lyimo TJ, Pol A, Harhangi HR, Jetten MSM, Op den Camp HJM. 2009. Anaerobic oxidation of dimethylsulfide and methanethiol in mangrove sediments is dominated by sulfate-reducing bacteria. *FEMS Microbiology Ecology* doi 10.1111/j.2574–6941. 2009. 00765x.

Lyimo TJ, Pol A, Op den Camp HJM, Harhangi HR, Vogels GD. 2000. *Methanosarcina semesiae* sp. nov., a dimethylsulfide-utilizing

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

methanogen from mangrove sediment. *International Journal of Sytematic and Evolutionary Microbiology* **50,** 171–178.

Malin G, Kirst GO. 1997. Algal production of dimethyl sulfide and its atmospheric role. *Journal of Phycology* **33,** 889–896.

Malin G, Wilson WH, Bratbak G, Liss PS, Mann NH. 1998. Elevated production of dimethylsulfhide resulting from viral infection of cultures of *Phaeocystis pouchetii*. *Limnology and Oceanography* **43,** 1389–1393.

McDevitt CA, Hugenholtz P, Hanson GR, McEwan AG. 2002. Molecular analysis of dimethyl sulphide dehydrogenase from *Rhodovulum sulfidophilum*: its place in the dimethyl sulphoxide reductase family of microbial molybdopterin-containing enzymes. *Molecular Microbiology* **44,** 1575–1587.

McEwan AG, Ferguson SJ, Jackson JB. 1991. Purification and properties of dimethyl sulphoxide reductase from *Rhodobacter capsulatus*. A periplasmic molybdoenzyme. *Biochemical Journal* **274,** 305–307.

McGrath SP, Zhao FJ. 1995. A risk assessment of sulphur deficiency in cereals using soil and atmospheric deposition data. *Soil Use and Management* **11,** 110–114.

McGugan WA. 2002. Cheddar cheese flavor. Review of current progress. *Journal of Agricultural and Food Chemistry* **23,** 1047–1050.

Meilgaard MC. 2002. Prediction of flavor differences between beers from their chemical composition. *Journal of Agricultural and Food Chemistry* **30,** 1009–1017.

Miers JC. 1966. Formation of volatile sulfur compounds in processed tomato products. *Journal of Agricultural and Food Chemistry* **14,** 419–423.

Miller TR, Hnilicka K, Dziedzic A, Desplats P, Belas R. 2004. Chemotaxis of *Silicibacter* sp. strain TM1040 toward dinoflagellate products. *Applied and Environmental Microbiology* **70,** 4692–4701.

Milo C, Reineccius GA. 1997. Identification and quantification of potent odorants in regular-fat and low-fat mild cheddar cheese. *Journal of Agricultural and Food Chemistry* **45,** 3590–3594.

Moosvi AS, McDonald IR, Pearce DA, Kelly DP, Wood AP. 2005. Molecular detection and isolation from Antarctica of methylotrophic bacteria able to grow with methylated sulfur compounds. *Systematic and Applied Microbiology* **28,** 541–554.

Moran MA, González JM, Kiene RP. 2003. Linking a bacterial taxon to sulfur cyling in the sea: studies of the marine *Roseobacter* group. *Geomicrobiolgy Journal* **20,** 375–388.

Neufeld JD, Boden R, Moussard H, Schäfer H, Murrell JC. 2008. Substrate-specific clades of active marine methylotrophs associated with a phytoplankton bloom in a temperate coastal environment. *Applied and Environmental Microbiology* **74,** 7321–7328.

Nguyen BC, Gaudry A, Bonsang B, Lambert G. 1978. Reevaluation of the role of dimethyl sulphide in the sulphur budget. *Nature* **275,** 637–639.

Ni SS, Boone DR. 1991. Isolation and characterization of a dimethyl sulfide-degrading methanogen, *Methanolobus siciliae* Hi350, from an oil-well, characterization of *M. siciliae* T4/Mt, and emendation of *M. siciliae*. *International Journal of Systematic Bacteriology* **41,** 410–416.

Noble R, Hobbs PJ, Dobrovin-Pennington A, Misselbrook TH, Mead A. 2001. Olfactory response to mushroom composting emissions as a function of chemical concentration. *Journal of Environmental Quality* **30,** 760–767.

Oelgeschlaeger E, Rother M. 2009. *In vivo* role of three fused corrinoid/methyl transfer proteins in *Methanosarcina acetivorans*. *Molecular Microbiology* **72,** 1260–1272.

Omori T, Saiki Y, Kasuga K, Kodama T. 1995. Desulfurization of alkyl and aromatic sulfides and sulfonates by dibenzothiophene-desulfurizing *Rhodococcus* sp strain SY1. *Bioscience Biotechnology and Biochemistry* **59,** 1195–1198.

Omura K, Swern D. 1978. Oxidation of alcohols by 'activated' dimethyl sulfoxide. A preparative, steric and mechanistic study. *Tetrahedron* **34,** 1651–1660.

Otte ML, Wilson G, Morris JT, Moran BM. 2004. Dimethylsulphoniopropionate (DMSP) and related compounds in higher plants. *Journal of Experimental Botany* **55,** 1919–1925.

Padden AN, Rainey FA, Kelly DP, Wood AP. 1997. *Xanthobacter tagetidis* sp. nov, an organism associated with *Tagetes* species and able to grow on substituted thiophenes. *International Journal of Systematic Bacteriology* **47,** 394–401.

Panter R, Penzhorn RD. 1980. Alkyl sulfonic acids in the atmosphere. *Atmospheric Environment* **14,** 149–151.

Papenbrock J, Riemenschneider A, Kamp A, Schulz-Vogt HN, Schmidt A. 2007. Characterization of cystein-degrading and H_2S-releasing enzymes of higher plants: from the field to the test tube and back. *Plant Biology* **9,** 582–588.

Parcell S. 2002. Sulphur in human nutrition and applications in medicine. *Alternative Medicine Review* **7,** 22–44.

Pearson TW, Dawson HJ, Lackey HB. 1981. Natural occurring levels of dimethyl sulphoxide in selected fruits, vegetables, grains, and beverages. *Journal of Agricultural and Food Chemistry* **29,** 1089–1091.

Pham M, Muller JF, Brasseur GP, Granier C, Megie G. 1995. A three-dimensional study of the tropospheric sulphur cycle. *Journal of Geophysical Research, Atmospheres* **100,** 26061–26092.

Plas C, Wimmer K, Jelinek E, Danner H, Holubar P, Harant H, Braun R. 1991. Microbial oxidation of carbondisulphide. *Medical Faculty Landbouwhoogeschool, University Gent* **56,** 575–577.

Pol A, Op den Camp HJM, Mees SGM, Kersten MASH, van der Drift C. 1994. Isolation of a dimethylsulfide-utilizing *Hyphomicrobium* species and its application in biofiltration of polluted air. *Biodegradation* **5,** 105–112.

Rammler DH, Zafferoni A. 1967. Biological implications of DMSO based on a review of its chemical properties. *Annals of the New York Academy of Science* **141,** 13–23.

Rappert S, Müller R. 2005. Odor compounds in waste gas emissions from agricultural operations and food industries. *Waste Management* **25,** 887–907.

Reichert K, Lipski A, Pradella S, Stackebrandt E, Altendorf K. 1998. *Pseudonocardia asaccharolytica* sp. nov. and *Pseudonocardia sulfidoxydans* sp. nov., two new dimethyl disulfide-degrading actinomycetes and emended description of the genus *Pseudonocardia*. *International Journal of Systematic Bacteriology* **48,** 441–449.

Rennenberg H. 1984. The fate of excess sulfur in higher plants. *Annual Review of Plant Physiology and Plant Molecular Biology* **35,** 121–153.

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

Rhoades JW. 2002. Coffee volatiles: analysis of the volatile constituents of coffee. *Journal of Agricultural and Food Chemistry* **8,** 136–141.

Richards SR, Kelly CA, Rudd JWM. 1991. Organic volatile sulphur in lakes of the Canadian Shield and its loss to the atmosphere. *Limnology and Oceanography* **36,** 468–482.

Ridgeway RG, Thornton DC, Bandy AR. 1992. Determination of trace aqueous dimethylsulphoxide concentrations by isotope-dilution gas-chromatography mass-spectrometry: application to rain and sea-water. *Journal of Atmospheric Chemistry* **14,** 53–60.

Saini HS, Attieh JM, Hanson AD. 1995. Biosynthesis of halomethanes and methanethiol by higher plants via a novel methyltransferase reaction. Plant*, Cell and Environment* **18,** 1027–1033.

Saltzman ES, Cooper DJ. 1989. Dimethyl sulfide and hydrogen sulfide in marine air. In: Saltzman ES, Cooper WJ, eds. *Biogenic sulfur in the environment*. ACS, 330–351.

Sambasivarao D, Scraba DG, Trieber C, Weiner JH. 1990. Organization of dimethyl sulfoxide reductase in the plasma membrane of *Escherichia coli*. *Journal of Bacteriology* **172,** 5938–5948.

Satoh T, Kurihara FN. 1987. Purification and properties of dimethylsulphoxide reductase containing a molybdenum cofactor from a photodenitrifier, *Rhodopseudomonas sphaeroides* f.s. *denitrificans*. *Journal of Biochemistry* **102,** 191–197.

Schäfer H. 2007. Isolation of *Methylophaga* spp. from marine dimethylsulfide-degrading enrichment cultures and identification of polypeptides induced during growth on dimethylsulfide. *Applied and Environmental Microbiology* **73,** 2580–2591.

Schmalenberger A, Hodge S, Bryant A, Hawkesford MJ, Singh BK, Kertesz MA. 2008. The role of *Variovorax* and other Comamonadaceae in sulfur transformations by microbial wheat rhizosphere communities exposed to different sulfur fertilization regimes. *Environmental Microbiology* **10,** 1486–1500.

Schmalenberger A, Hodge S, Hawkesford MJ, Kertesz MA. 2009. Sulfonate desulphurization in *Rhodococcus* from wheat rhizosphere communities. *FEMS Microbiology Ecology* **67,** 140–150.

Scholten JCM, Kelly DP, Murrell JC. 2003. Growth of sulfate-reducing bacteria and methanogenic archaea with methylated sulfur compounds: a commentary on the thermodynamic aspects. *Archives of Microbiology* **179,** 135–144.

Schnug E, Booth E, Haneklaus S, Walker KC. 1995. Sulphur supply and stress resistance in oilseed rape. In: *Proceedings of the 9th International Rapeseed Congress, Cambridge,* 1995, 229–231.

Schröder P. 1993. Plants as sources of atmospheric sulfur. In: De Kok LJ, Stulen I, Rennenberg H, Brunold C, Rauser WE, eds. *Sulfur nutrition and assimilation in higher plants: regulatory, agricultural and environmental aspects*. The Hague, The Netherlands: SPB Academic Publishing, 253–270.

Sciare J, Baboukas E, Hancy R, Mihalopoulos N, Nguyen BC. 1998. Seasonal variation of dimethylsulfoxide in rainwater at Amsterdam island in the southern Indian Ocean: implications on the biogenic sulphur cycle. *Journal of Atmospheric Chemistry* **30,** 229–240.

Segurel MA, Razungles AJ, Riou C, Salles M, Baumes RL. 2004. Contribution of dimethyl sulfide to the aroma of syrah and grenache noir wines and estimation of its potential in grapes of these varieties. *Journal of Agricultural and Food Chemistry* **52,** 7084–7093.

Shaw PE, Ammons JM, Braman RS. 1980. Volatile sulfur compounds in fresh orange and grapefruit juices: identification, quantitation, and possible importance to juice flavor. *Journal of Agricultural and Food Chemistry* **28,** 778–781.

Shu CH, Chen CK. 2009. Enhanced removal of dimethyl sulfide from a synthetic waste gas stream using a bioreactor inoculated with *Microbacterium* sp NTUT26 and *Pseudomonas putida*. *Journal of Industrial Microbiology and Biotechnology* **36,** 95–104.

Sivelä S, Sundman V. 1975. Demonstration of *Thiobacillus*-type bacteria, which utilize methyl sulfides. *Archives of Microbiology* **103,** 303–304.

Smet E, Chasaya G, VanLangenhove H, Verstraete W. 1996. The effect of inoculation and the type of carrier material used on the biofiltration of methyl sulphides. *Applied Microbiology and Biotechnology* **45,** 293–298.

Smith NA. 1987. Metabolism of dimethyl disulfide, carbon disulfide and other volatile sulfur compounds by chemolithoautotrophic sulfur bacteria. PhD thesis, University of Warwick, Coventry.

Smith NA, Kelly DP. 1988. Isolation and physiological characterization of autotrophic sulfur bacteria oxidizing dimethyl disulfide as sole source of energy. *Journal of General Microbiology* **134,** 1407–1417.

Sorokin DY, Jones BE, Kuenen JG. 2000. An obligate methylotrophic, methane-oxidizing *Methylomicrobium* species from a highly alkaline environment. *Extremophiles* **4,** 145–155.

Stefels J. 2000. Physiological aspects of the production and conversion of DMSP in marine algae and higher plants. *Journal of Sea Research* **43,** 183–197.

Steudler PA, Peterson BJ. 1984. Contribution of gaseous sulfur from salt marshes to the global sulfur cycle. *Nature* **311,** 455–457.

Styrvold OB, Strom AR. 1984. Dimethylsulfoxide and trimethylamine oxide respiration of *Proteus vulgaris*: evidence for a common terminal reductase system. *Archives of Microbiology* **140,** 74–78.

Sunda W, Kieber DJ, Kiene RP, Huntsman S. 2002. An antioxidant function for DMSP and DMS in marine algae. *Nature* **418,** 317–320.

Suylen GMH, Kuenen JG. 1986. Chemostat enrichment and isolation of *Hyphomicrobium* EG a dimethyl sulfide oxidizing methylotroph and reevaluation of *Thiobacillus* MS1. *Antonie Van Leeuwenhoek* **52,** 281–293.

Suylen GMH, Large PJ, Vandijken JP, Kuenen JG. 1987. Methyl mercaptan oxidase, a key enzyme in the metabolism of methylated sulfur-compounds by *Hyphomicrobium* EG. *Journal of General Microbiology* **133,** 2989–2997.

Tallant TC, Krzycki JA. 1997. Methylthiol:Coenzyme M methyltransferase from *Methanosarcina barkeri*, an enzyme of methanogenesis from dimethylsulfide and methylmercaptopropionate. *Journal of Bacteriology* **179,** 6902–6911.

Talou T, Delmas M, Gaset A. 1987. Principal constituents of black truffle (*Tuber melanosporum*) aroma. *Journal of Agricultural and Food Chemistry* **35,** 774–777.

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

Talou T, Gaset A, Delmas M, Kulifaj M, Montant C. 1990. Dimethyl sulfide: the secret for black truffle hunting by animals. *Mycological Research* **94,** 277–278.

Tanimoto Y, Bak F. 1994. Anaerobic degradation of methylmercaptan and dimethyl sulfide by newly isolated thermophilic sulfate-reducing bacteria. *Applied and Environmental Microbiology* **60,** 2450–2455.

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.

Todd JD, Rogers R, Li YG, Wexler M, Bond PL, Sun L, Curson ARJ, Malin G, Steinke M, Johnston AWB. 2007. Structural and regulatory genes required to make the gas dimethyl sulfide in bacteria. *Science* **315,** 666–669.

Ulrich D, Hoberg E, Bittner T, Engewald W, Meilchen K. 2001. Contribution of volatile compounds to the flavor of cooked asparagus. *European Food Research and Technology* **213,** 200–204.

Vallina SM, Simó R. 2007. Strong relationship between DMS and the solar radiation dose over the global surface ocean. *Science* **315,** 506–508.

Vallina SM, Simó R, Gassó S. 2006. What controls CCN seasonality in the Southern Ocean? A statistical analysis based on satellite-derived chlorophyll and CCN and model-estimated OH radical and rainfall. *Global Biogeochemical Cycles* **20,** GB1014.

Vallina SM, Simó R, Manizza M. 2007. Weak response of oceanic dimethylsulfide to upper mixing shoaling induced by global warming. *Proceedings of the National Academy of Sciences, USA* **104,** 16004–16009.

Van Alstyne KL, Puglisi MP. 2007. DMSP in marine macroalgae and macroinvertebrates: distribution, function, and ecological impacts. *Aquatic Sciences* **69,** 394–402.

Vila-Costa M, Del Valle DA, González JM, Slezak D, Kiene RP, Sánchez O, Símo R. 2006. Phylogenetic identification and metabolism of dimethylsulfide degrading marine bacteria. *Environmental Microbiology* **8,** 2189–2200.

Visscher PT, Baumgartner LK, Buckley DH, Rogers DR, Hogan ME, Raleigh CD, Turk KA, Des Marais DJ. 2003. Dimethyl sulfide and methanethiol formation in microbial mats: potential pathways for biogenic signatures. *Environmental Microbiology* **5,** 296–308.

Visscher PT, Quist P, van Gemerden H. 1991. Methylated sulfur compounds in microbial mats: *in situ* concentrations and metabolism by a colorless sulfur bacterium. *Applied and Environmental Microbiology* **57,** 1758–1763.

Visscher PT, Taylor BF. 1993*a*. Aerobic and anaerobic degradation of a range of alkyl sulfides by a denitrifying marine bacterium. *Applied and Environmental Microbiology* **59,** 4083–4089.

Visscher PT, Taylor BF. 1993*b*. A new mechanism for the aerobic catabolism of dimethyl sulfide. *Applied and Environmental Microbiology* **59,** 3784–3789.

Visscher PT, van Gemerden H. 1991. Photo-autotrophic growth of *Thiocapsa roseopersicina* on dimethyl sulfide. *FEMS Microbiology Letters* **81,** 247–250.

Vogt C, Rabenstein A, Rethmeier J, Fischer U. 1997. Dimethyl sulfoxide reduction with reduced sulphur compounds as electron donors by anoxygenic phototrophic bacteria. *Microbiology* **143,** 767–773.

Vohra J. 2000. Physiological, biochemical and molecular characterization of novel methylotrophs isolated from the foot. MSc thesis, King's College, London (UK).

Watson AJ, Upstill-Goddard RC, Liss PS. 1991. Air–sea gas exchange in rough and stormy seas measured by a dual-tracer technique. *Nature* **349,** 145–147.

Watts SF. 2000. The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide. *Atmospheric Environment* **34,** 761–779.

Weiner JH, Rothery RA, Sambasivarao D, Trieber CA. 1992. Molecular analysis of dimethylsulfoxide reductase: a complex iron–sulfur molybdoenzyme of *Escherichia coli*. *Biochimica et Biophysica Acta (BBA) - Bioenergetics* **1102,** 1–18.

Williams J, Holzinger R, Gros V, Xu X, Atlas E, Wallace DWR. 2004. Measurements of organic species in air and seawater from the tropical Atlantic. *Geophysical Research Letters* **31,** L23S06.

Wolfe GV, Steinke M. 1996. Grazing-activated production of dimethyl sulfide (DMS) by two clones of *Emiliania huxleyi*. *Limnology and Oceanography* **41,** 1151–1160.

Wolfe GV, Sherr EB, Sherr BF. 1994. Release and consumption of DMSP from *Emiliania huxleyi* during grazing by *Oxyrrhis marina*. *Marine Ecology Progress Series* **111,** 111–119.

Wong FF, Carson JF. 1966. Isolation of *S*-methyl methionine sulfonium salt from fresh tomatoes. *Journal of Agricultural and Food Chemistry* **14,** 247–249.

Yamamoto I, Wada N, Ujiiye T, *et al*. 1995. Cloning and nucleotide-sequence of the gene encoding dimethyl-sulfoxide reductase from *Rhodobacter sphaeroides* f. sp. *denitrificans*. *Bioscience Biotechnology and Biochemistry* **59,** 1850–1855.

Yoch DC. 2002. Dimethylsulfoniopropionate: its sources, role in the marine food web, and biological degradation to dimethylsulfide. *Applied and Environmental Microbiology* **68,** 5804–5815.

Yoch DC, Carraway RH, Friedman R, Kulkarni N. 2001. Dimethylsulfide (DMS) production from dimethylsulfoniopropionate by freshwater river sediments: phylogeny of Gram-positive DMS-producing isolates. *FEMS Microbiology Ecology* **37,** 31–37.

Zeyer J, Eicher P, Wakeham SG, Schwarzenbach RP. 1987. Oxidation of dimethyl sulfide to dimethyl sulfoxide by phototrophic bacteria. *Applied and Environmental Microbiology* **53,** 2026–2032.

Zhang L, Hirai M, Shoda M. 1991*a*. Removal characteristics of dimethyl sulfide, methanethiol and hydrogen-sulfide by *Hyphomicrobium* sp. 155 isolated from peat biofilter. *Journal of Fermentation and Bioengineering* **72,** 392–396.

Zhang L, Kuniyoshi I, Hirai M, Shoda M. 1991*b*. Oxidation of dimethyl sulfide by *Pseudomonas acidovorans* DMR-11 isolated from a peat biofilter. *Biotechnology Letters* **13,** 223–228.

Zhao FJ, Knights JS, Hu ZY, McGrath SP. 2003. Stable sulfur isotope ratio indicates long-term changes in sulfur deposition in the Broadbalk experiment since 1845. *Journal of Environmental Quality* **32,** 33–39.

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022

Zhu JY, Chai XS, Pan XJ, Luo Q, Li J. 2002. Quantification and reduction of organic sulfur compound formation in a commercial wood pulping process. *Environmental Science and Technology* **36,** 2269–2272.

Zhu L, Nicovich JM, Wine PH. 2003. Temperature-dependent kinetics studies of aqueous phase reactions of hydroxyl radicals with dimethylsulfoxide, dimethylsulfone, and methanesulfonate. *Aquatic Sciences* **65,** 425–435.

Zinder SH, Brock TD. 1978*a*. Dimethyl sulfoxide as an electron acceptor for anaerobic growth. *Archives of Microbiology* **116,** 35–40.

Zinder SH, Brock TD. 1978*b*. Production of methane and carbon dioxide from methane thiol and dimethyl sulfide by anaerobic lake sediments. *Nature* **273,** 226–228.

Zinder SH, Brock TD. 1978*c*. Dimethyl sulfoxide reduction by microorganisms. *Journal of General Microbiology* **105,** 335–342.

Downloaded from https://academic.oup.com/jxb/article/61/2/315/620009 by guest on 21 August 2022