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Review

Microbial cycling of volatile organic sulfur compounds

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Abstract. Microbial cycling of volatile organic sulfur compounds (VOSCs), especially dimethyl sulfide (DMS) and methanethiol (MT), is intensively studied because these compounds play an important role in the processes of global warming, acid precipitation, and the global sulfur cycle. VOSC concentrations in freshwater sediments are low due to the balance between the formation and degradation of these compounds. These reactions occur for the greater part at the oxic/anoxic interphase of sediment and water column. In contrast to marine ecosystems, where dimethylsulfoniopropionate is the main precursor of MT and DMS, in freshwater ecosystems, VOSCs are formed mainly by methylation of sulfide and to a lesser extent from the degradation of S-containing amino acids. One of the major routes for DMS and MT formation through sulfide methylation is anaerobic *O*-demethylation of methoxylated aromatic compounds. Inhibition studies have revealed that the major part of the endogenously produced MT and DMS is degraded anaerobically by methanogens. The major bacterial groups involved in formation and consumption of VOSCs are described.

Key words. Dimethyl sulfide; methanethiol; volatile sulfur compounds; freshwater; sulfur cycle; sediment.

Introduction

The element sulfur occurs in an extremely large variety of oxidation states (table 1). These range from completely reduced (oxidation state –2) to completely oxidized (oxidation state +6). However, only three of these oxidation states are abundant in nature: –2 in the form of sulfhydryl and sulfide, 0 in the form of elemental sulfur, and +6 in the form of sulfate. These compounds are continuously converted into each other by a combination of biological, chemical, and geochemical processes (fig. 1). The conversions of the inorganic sulfur compounds and to a lesser extent also those of the organic sulfur compounds are dominated by microbiological transformations [1–4]. The combination of these processes results in the global sulfur cycle (fig. 2). The complexity of the sul-

Table 1. Various species of sulfur compounds.

Component	Appearance	Oxidation state
Hydrogen sulfide	H_2S/HS^-	–2
Reduced organic sulfur compounds	mercaptans, carbonyl- and methylsulfides	–2
Metal sulfides	FeS, FeS_2	–2
Pyretic sulfur	(S_2^{2-})	–1
Elemental sulfur	S	0
Thiosulfate	$S_2O_3^{2-}$	+2
Tetrathionate	$S_4O_6^{2-}$	$+2^1/_2$
Dithionite	$S_2O_4^{2-}$	+3
Sulfur dioxide	SO_2	+4
Sulfite	SO_3^{2-}	+4
Sulfate	SO_4^{2-}	+6
Sulfur polymers		
Polysulfanes	$H\text{-}S_n\text{-}H$ (n = 1–35)	
Polysulfides	S_n^{2-} (n = 1–8)	
Organic polysulfanes	$R\text{-}S_n\text{-}R$ (n = 1–35)	
Polythionates	$^-O_3S\text{-}S_n\text{-}SO_3^-$ (n = 1–22)	
Polysulfur	S_∞ (>10^5)	

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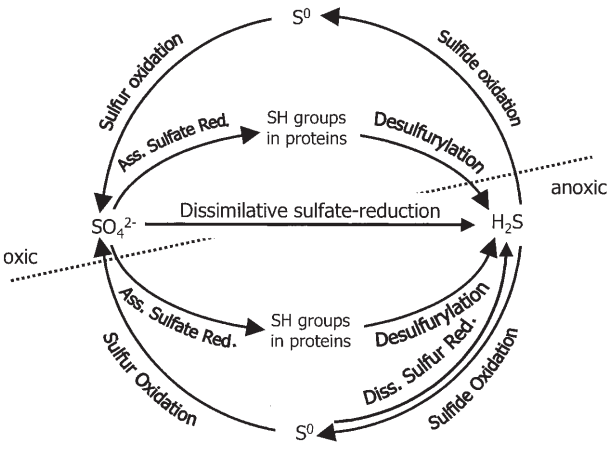

Figure 1. Redox cycle of sulfur.

fur cycle is even higher if one realizes that the cycle is strongly linked to that of other elements like carbon, nitrogen, and iron through various biological and (geo)chemical processes. The major part of the Earth's sulfur is deposited in sediment and rocks as gypsum ($CaSO_4$) and pyrite (FeS_2) and in oceans as sulfate. Another large part is incorporated into biomass as S-containing compounds like S-containing amino acids.

Reduction of sulfate and sulfite can be either assimilatory for the synthesis of organic sulfur compounds or dissimilatory in order to dispose of an excess of reduction equivalents. The sulfide produced can be either deposited as metal sulfides, or it can be oxidized to elemental sulfur or sulfate. Sulfide can also be methylated both chemically or biologically to (volatile) organic compounds. The microbial and biogeochemical cycling of these organic sulfur compounds with special emphasis on volatile (organic) sulfur compounds [V(O)SCs] in freshwater systems forms the subject of this review.

Global significance of VOSCs

In the global sulfur cycle, VSCs connect the atmospheric with the terrestrial, oceanic, estuarine, and freshwater compartments. The global significance of VOSCs became clear when low but significant amounts of dimethyl sulfide (DMS) were detected in ocean waters [6]. This led to the general assumption that DMS is the 'missing link' in the global sulfur cycle connecting the ocean with the atmosphere compartment. Until then, the assumption had been that the sulfur emission from the oceans to the atmosphere consisted mainly of H_2S [7]. Sulfide concentrations in ocean surface water sufficiently high to confirm its possible role in the global sulfur cycle, however, had never been detected. According to the new hypothesis, sulfur is transferred as DMS via the atmosphere (primarily as oxidation products of DMS) to terrestrial systems where it is deposited through rain precipitation (fig. 2) [7]. Since this finding, research on the microbiology, chemistry, and biogeochemistry of these organic sulfur compounds has been intensified. In 1987, a model was proposed [8], which stated that increased global temperatures will result in an increased production of DMS due to a higher primary production of dimethylsulfoniopropionate (DMSP), an osmolyte in marine algae and a precursor of DMS, and consequently to higher atmospheric DMS emission rates (fig. 3). Enhanced atmospheric DMS concentrations will subsequently result in higher atmospheric concentrations of its oxidation products, which act as cloud condensation nuclei. Higher concentrations of these nuclei will result in a denser cloud albedo, reducing the amount of sunlight that reaches the Earth's surface and consequently reducing global temperature. This drop in temperature is suggested to cause a decrease in the primary production of DMSP

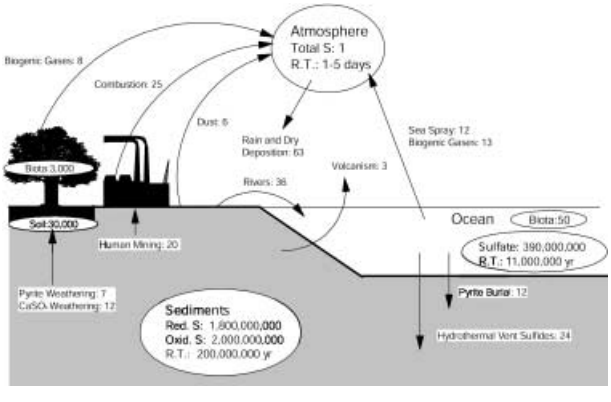

Figure 2. Global biogeochemical cycle of sulfur. All reservoirs are given in 10^{11} mol S and all fluxes (arrows) in 10^{11} mol S per year. R.T. is residence time. This figure is used with permission from Middelburg [5].

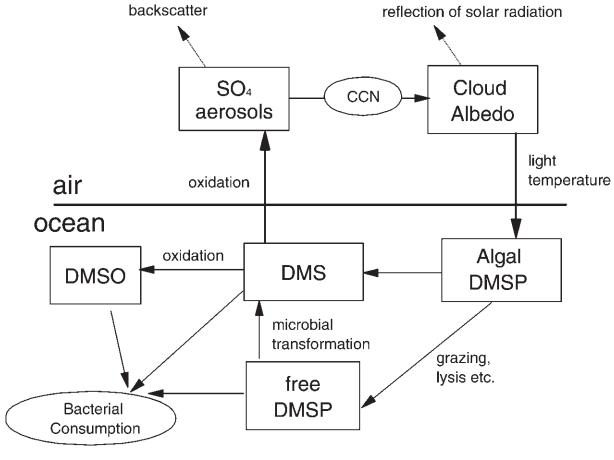

Figure 3. Simplified scheme illustrating the processes that link the biogeochemical cycle of DMS with climate (ccc, cloud condensation nuclei). This figure is used with permission from Middelburg [5].

Table 2. Emission rates of V(O)SCs from natural and anthropogenic sources to the atmosphere [2].

Source	Sulfur compound release (Tg year^{-1})						
	SO_2	H_2S	DMS	DMDS	CS_2	COS	Total
Oceanic		0–15	38–40	0–1	0.3	0.4	38.7–56.7
Salt marsh		0.8–0.9	0.58	0.13	0.07	0.12	1.7–1.8
Swamps		11.7	0.84	0.2	2.8	1.85	17.4
Soil and plants		3–41	0.2–4.0	1	0.6–1.5	0.2–1.0	5.0–48.5
Burning of biomass	7	0–1		0–1		0.11	7.1–9.1
Volcanoes/fumeroles	8	1		0–0.02	0.01	0.01	9.0
Total	15	16.5–70.6	39.6–45.4	1.3–3.4	3.8–4.7	2.7–3.5	78.9–142.6

(in other words DMS). Thus, DMS was considered to be counteractive to the behavior of greenhouse gases like methane and carbon dioxide.

Annually, vast amounts of DMS (75% of total sulfur flux) and other V(O)SCs (e.g., H_2S and COS/CS_2, representing 15 and 10% of the total sulfur flux, respectively) are released into the atmosphere by a combination of anthropogenic, geochemical, and biological processes (table 2). V(O)SCs cause environmental problems on local and regional scales. Of major concern is the release of (in)organic sulfur compounds due to anthropogenic activities causing the acidification of forests and lakes. Locally, V(O)SCs are notorious for their odor problems [9, 10]. Whereas at low concentrations they are important flavor components (e.g., in beer and cheese), at higher concentrations, V(O)SCs are very toxic (table 3). Large amounts of V(O)SCs are released by composting plants, wastewater treatment plants [14], and paper and textile industries [15]. Only a minor fraction of the DMS formed biologically reaches the atmosphere [16]. About 90% of the DMS produced is degraded by anaerobic and aerobic microbes before it can be ventilated to the atmosphere. Microbial conversions therefore effectively control the fluxes of VOSCs from natural systems to the atmosphere. Furthermore, combustion of sulfur-containing fossil fuels contributes to a large extent to the total emission of SO_2 into the atmosphere.

The impact of environmental factors on the delicate balance between VOSC-forming, VOSC-degrading, and VOSC ventilation processes, however, is not well understood. Since DMS and methanethiol (MT) appear to be the major VOSCs in most natural systems, the formation and degradation of these compounds will be discussed in more detail.

Table 3. Properties of some volatile sulfur compounds, derived from Bhatia [11], Suylen [12] and the Merck Index [13].

Compound	LD_{50} (ppm)	MAC (ppm)	Odor threshold (ppm)
H_2S	444	10	8.5–1000
MT	675	0.5	0.9–8.5
DMS	40250	20	0.6–40
DMDS	5	< 20	0.1–3.6

Lethal concentrations are expressed as LD_{50}. MAC, maximal acceptable concentration; MT, methanethiol.

Microbial production of VOSCs

Several mechanisms for the microbial formation of VOSCs have been identified (table 4). Formation of MT and DMS has been reported to originate from S-containing amino acids under both aerobic and anaerobic conditions [17–20]. Methionine is first deaminated and subsequently demethylated to α-ketobutyrate, ammonia, and MT. This degradation of methionine and several methionine derivatives is catalyzed by the commonly occurring enzyme L-methionine γ-lyase. Similarly, S-methyl-cysteine is degraded by S-alkylcysteinase resulting in the formation of pyruvate, ammonia, and MT. Conversion of S-methyl-methionine mainly results in the formation of DMS [21], whereas degradation of cysteine results in the formation of H_2S. The MT formed is chemically oxidized to dimethyl disulfide (DMDS) [2].

In marine, estuarine, and salt marsh systems, formation of MT and DMS originates mainly from the degradation of DMSP, an osmolyte in many algae, dinoflagellates, coccolithophores, and halophilic plants species [22–25]. DMSP can be degraded to acrylate and DMS by DMSP-lyase [26]. This cleavage has been demonstrated for several aerobic and anaerobic bacteria [22, 26–34], phytoplankton [25, 35–39], flowering plants [22, 40], and marine fungi [41]. Alternatively, DMSP can be aerobically or anaerobically demethylated to form 3-methylmercaptopropionate [30, 42–48]. Subsequently, this compound can be either demethiolated, resulting in the formation of MT and propionate, or demethylated, resulting in the formation of 3-mercaptopropionate [48, 49]. The latter compound can be further degraded both aerobically and anaerobically [42, 43, 48].

Another commonly occurring mechanism of DMS formation is the reduction of dimethylsulfoxide (DMSO). Significant amounts of DMSO (1–200 nM), which prob-

Table 4. Microbial mechanisms for VOSC degradation and production.

Mechanism	Reaction		
VOSC formation			
DMSP cleavage	DMSP	→	acrylate + DMS
MMPA demethiolation	MMPA	→	acrylate + MT
S-amino acid degradation	S-AA	→	HS^-/MT/DMS + AA
DMSO reduction	lactate + DMSO	→	DMS + acetate
Sulfide methylation			
detoxification	HS^- + R-CH_3	→	R_a + MT
MA degradation	HS^- + R-CH_3	→	R_b + MT
	MT + R-CH_3	→	R_b + DMS
DMDS oxidation/reduction	DMDS	← →	2 MT
VOSC degradation			
Oxidation	DMS/MT + O_2	→	MT + CH_2O → CO_2 + SO_4^{2-}
	DMS/MT + O_2	→	CO_2 + $S_2O_3^{2-}$
Phototrophic oxidation	DMS/MT	→	DMSO
Oxidation to DMSO	DMS + O_2	→	DMSO
Denitrification	DMS/MT + NO_3^-	→	N_2 + CO_2 + SO_4^{2-}
Methanogensis	DMS/MT	→	CH_4 + CO_2 + HS^-
Sulfate reduction	DMS/MT + SO_4^{2-}	→	CO_2 + HS^-

MA, methoxylated aromatic compounds; DMSP, dimethylsulfoniopropionate; MMPA, methylmercaptopropionate; S-AA, sulfur-containing amino acids; AA, amino acids; MA, methoxylated aromatic compounds; DMSO, dimethylsulfoxide; R, variable residue, group, or compound; DMDS, dimethyl disulfide.

ably originate from marine phytoplankton, have been found in ocean surface waters [50]. DMSO-reducing capacity was found to be widespread among aerobic and anaerobic bacteria, plants, and animals [51–53]. However, the relevance of DMSO reduction as a source of DMS in situ remains unclear.

Reduction of DMDS can also give rise to MT formation. From incubations with sediment slurries amended with DMDS, Kiene et al. [54] concluded that DMDS is reduced to MT. Subsequently, MT is metabolized to methane. Drotar et al. [55] and Larsen [56] showed that MT is also formed by methylation of sulfide by various bacteria from different habitats. This methylation, which is mediated by sulfide-dependent thiol methyltransferases, is probably a detoxification pathway for sulfide and appeared to be restricted to aerobic microorganisms. Methylation of MT resulting in the formation of DMS by these organisms was not observed.

Several authors have observed formation of MT and DMS during degradation of methoxylated aromatic compounds and concluded that this is caused by the methylation of sulfide and MT [57–60]. Differences in lag phases between marine (2–3 days) and freshwater sediments (no clear lag phase) before MT or DMS started to accumulate suggest that these methoxylated aromatic compounds are especially important precursors for MT and DMS in freshwater systems. Various anaerobic bacteria performing sulfide-mediated *O*-demethoxylation, which results in VOSC formation, have now been isolated from various habitats (table 5). In contrast to other previously isolated homoacetogenic bacteria, which transfer the methyl groups of methoxylated aromatic compounds to CO to produce acetate [61, 68], these organisms can also use sulfide and MT as the methyl group acceptors, resulting in the formation of MT and DMS, respectively (fig. 4, table 5) [69, 70]. The hydroxylated aromatic residue obtained after demethylation is degraded via the phloroglucinol pathway to acetate or a combination of acetate and butyrate (fig. 4) [69]. Since methoxylated aromatic compounds are degradation products of lignin, a highly abundant biopolymer on earth, this mechanism for VOSC production is likely to be important in freshwater systems that are generally more organic rich than

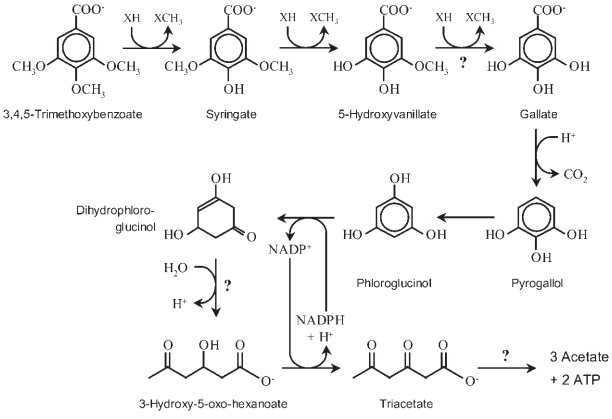

Figure 4. Pathway of 3,4,5-trimethoxybenzoate degradation by *Holophaga foetida* strain TMBS 4. The sequential demethylation of 3,4,5-trimethoxybenzoate is followed by the degradation of the hydroxylated residue via the phloroglucinol pathway. X may represent OH, SH, or SCH_3. Question marks indicate reactions that have not yet been elucidated. This figure was used with permission of Kreft and Schink [69].

Table 5. Characteristics of bacteria performing anaerobic methylation of sulfide and homoacetogenesis during degradation of syringate and 3,4,5-trimethoxybenzoate.

Bacterium	Products from		References
	methoxy groups	aromatic residue	
Acetobacterium woodii	acetate	not degraded	[61]
Sporomusa ovata	acetate	not degraded	[62]
Clostridium thermoaceticum	acetate	not degraded	[63]
Strain SS1	acetate	not degraded	[64]
Holophaga foetida	DMS, MT, or acetate	acetate	[57]
Sporobacter termitidis	DMS, MT, or acetate	acetate	[65]
Sporobacterium olearium	DMS, MT, or acetate	acetate	[66]
Strain SA2	DMS, MT	acetate, butyrate	[57]
Parasporobacterium paucivorans	DMS, MT	acetate, butyrate	[67]

marine and estuarine systems. The degradation of lignin is an aerobic process [71] and these compounds therefore likely occur in the anaerobic/aerobic interphase.

Microbial degradation of VOSCs

Although VOSCs are produced continuously in the biosphere, concentrations in the atmosphere are relatively constant, which indicates that considerable sinks for VOSCs must exist. So far, several mechanisms have been found to result in a consumption of VOSCs in the biosphere. Besides processes like ventilation to the atmosphere, chemical oxidation, and the adhesion to particles followed by sedimentation or transport to the deep sea, VOSCs were found to be converted through microbial degradation [3, 4, 16]. Comparison of the residence times of the different processes [16, 72] showed that rates of microbial degradation are high compared to that of the other processes. Therefore, microbial degradation will have a dramatic impact on the different fluxes within the sulfur cycle. Microbial degradation has been demonstrated to occur both aerobically and anaerobically. A variety of aerobic microorganisms able to degrade MT and DMS (and DMSO) have been isolated from sewage treatment plants, marine sediments, soil, and biofilters. The isolates mainly belong to the genera *Thiobacillus*, *Methylophaga,* and *Hyphomicrobium* [12, 15, 73–81]. The mechanism for DMS degradation has been elucidated for several *Hyphomicrobium* and *Thiobacillus* strains [75, 79]. *Hyphomicrobium* strains also reduce DMSO to DMS by the action of an NADH-dependent reductase. DMS is oxidized by a monooxygenase to MT and formaldehyde. MT is subsequently oxidized by MT oxidase, which results in the formation of formaldehyde, hydrogen peroxide, and sulfide (fig. 5). The oxidation of sulfide yields sulfuric acid. Part of the formaldehyde produced is incorporated into cell biomass through the serine pathway. Hyphomicrobia are therefore known as C_1-compound-metabolizing heterotrophs. In contrast to hyphomicrobia, thiobacilli are generally known to be chemolithoautotrophs. However, cultivation experiments revealed that besides sulfide oxidation they are also capable of oxidation of VOSCs [74, 78]. Oxidation of DMS also resulted in the formation of sulfide and formaldehyde, which are further oxidized to sulfuric acid and car-

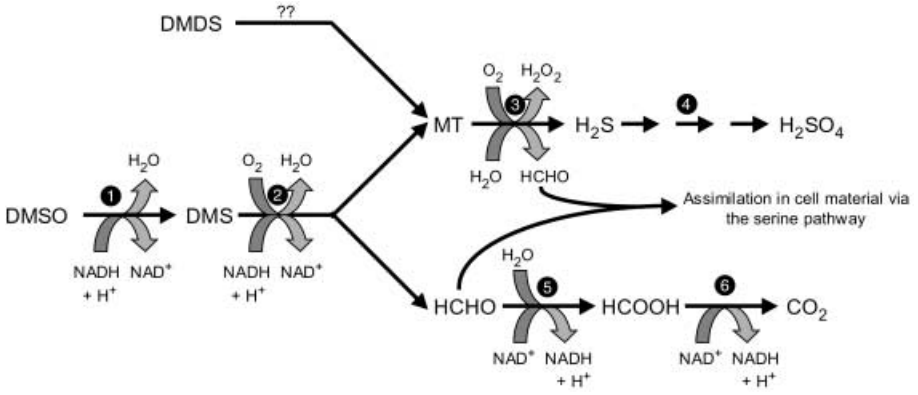

Figure 5. Mechanism for degradation of DMDS, DMSO, DMS, MT, and H_2S by *Hyphomicrobium* S [71]. Symbols: ❶, DMSO reductase; ❷, DMS monooxygenase; ❸, MT oxidase; ❹, sulfide-oxidizing enzymes; ❺, formaldehyde dehydrogenase; ❻, formate dehydrogenase. Question marks indicate reactions that have not yet been elucidated.

bon dioxide. *Thiobacillus* strains use the Calvin cycle to fix carbon dioxide. From a tidal sediment, an obligate methylotroph, *Methylophaga sulfidovorans*, was isolated which converted DMS to carbon dioxide and thiosulfate [76]. This heterotrophic bacterium, which uses the ribulose monophosphate route for carbon assimilation, can also use sulfide as an additional energy source.

Furthermore, a large variety of bacteria are capable of oxidizing DMS to DMSO, provided an additional carbon source is present [82]. The oxidation is carried out by monooxygenases that are widespread among animals, plants, fungi, and bacteria [50, 83]. Further oxidation of DMSO to dimethylsulfone by haloperoxidases has been found in several marine microorganisms [84].

Anaerobic degradation of DMS and MT has been mainly attributed to the activity of methanogens, sulfate-reducing bacteria, anoxygenic phototrophs, and denitrifying bacteria [3, 4, 54, 79, 85–87]. Anoxygenic phototrophic sulfur bacteria, which normally use sulfide as an electron donor, can oxidize DMS to DMSO with DMS as electron donor [88, 89]. This mechanism of DMS degradation is very important in microbial mats of intertidal sediments where light is abundant during low tide.

Methanogenic conversion of MT and DMS was first illustrated in lake sediment slurries in which ^{14}C-DMS was converted to ^{14}C-methane and ^{14}C-carbon dioxide [3, 4]. Upon addition of chloroform, an inhibitor of the methyltransferase reactions in methanogens, production of ^{14}C-methane was inhibited whereas ^{14}C-carbon dioxide formation was not. From inhibitor studies with marine and estuarine sediments, Kiene et al. [54] concluded that methanogenic and sulfate-reducing bacteria competed for DMS at concentrations lower than 10 μM, while methanogens dominated DMS degradation at higher concentrations. Methanogens reduce DMS to methane and MT, and the latter is subsequently disproportionated to methane, carbon dioxide, and H_2S (tables 4, 6). The excess of reduction equivalents released during this disproportionation is used for the initial reduction of DMS. In this way, 2 mol of DMS are stoichiometrically converted to 3 mol of methane and 1 mol of carbon dioxide. Several methanogens able to use DMS have been isolated from marine, estuarine, and salt lake habitats [54, 85, 90; see also table 7], but the first DMS-utilizing freshwater strain was only isolated recently [91]. This isolate was an obligately methylotrophic methanogen, *Methanomethylovorans hollandica*, which belonged to a novel genus [91]. With the use of amplified ribosomal DNA restriction analysis and 16S rRNA gene sequence analysis, this methanogen was found to be a common inhabitant of Dutch freshwater sediments [92]. Recently, similar methanogens were found in Victoria lake (Tanzania) sediment (unpublished observations). Moreover, our studies have shown that methanogenesis is a major sink for DMS and MT in freshwater sediments [91, 92]. The initial suggestion was that MT could only be cometabolized by methanogens in the presence of DMS. However, many of the DMS-degrading methanogens were later demonstrated to grow also on MT as sole carbon and energy source [85, 93, 94]. MT is disproportionated in the same way as methanol (table 6). Methylated sulfur compounds have also been found to serve as a sulfur source in several methanogens incapable of methane formation from them compounds [90].

Table 6. Conversion of methanogenic substrates.

Reaction equations			$\Delta G^{0'}$ (KJ/mol CH_4)
$CO_2 + 4H_2$	→	$CH_4 + 2H_2O$	−130.4
$4HCOOH$	→	$CH_4 + 3CO_2 + 2\ H_2O$	−119.5
$4CO + 2H_2O$	→	$CH_4 + 3CO_2$	−185.5
CH_3COOH	→	$CH_4 + CO_2$	−36.0
$4CH_3OH$	→	$3CH_4 + CO_2 + 2H_2O$	−106.0
$CH_3OH + H_2$	→	$CH_4 + H_2O$	−112.5
$4CH_3NH_2 + 2H_2O$	→	$3CH_4 + CO_2 + 4NH_3$	−76.7
$2(CH_3)_2NH + 2H_2O$	→	$3CH_4 + CO_2 + 2NH_3$	−74.8
$4(CH_3)_3N + 6H_2O$	→	$9CH_4 + 3CO_2 + 4NH_3$	−75.8
$4CH_3SH + 2H_2O$	→	$3CH_4 + CO_2 + 4H_2S$	−51.0
$2(CH_3)_2S + 2H_2O$	→	$3CH_4 + CO_2 + 2H_2S$	−52.2

Evidence for the possible role of sulfate-reducing bacteria in the degradation of DMS and MT mainly originates from inhibitor studies with molybdate and tungstate [19, 86]. These compounds competitively inhibit sulfate reduction and therefore should be added in equal or higher amounts than the ambient sulfate concentrations. This poses no problems for freshwater systems in which sulfate concentrations are generally below 2 mM. However, in marine, estuarine, and salt lake systems, molybdate concentrations of 20 mM or higher are needed. Such high concentrations of molybdate also inhibited methanogenesis in freshwater sediments [95]. Molybdate and tungstate are also known as cofactors for a number of enzymes and might therefore also influence the activity of microorganisms other than sulfate-reducing bacteria. Moreover, since molybdate forms complexes with sulfides it can effectively lower the free sulfide, concentrations and thereby affect the redox potential as well as the activity of microbes that require sulfide as a sulfur source. Despite the considerable evidence of the possible role of sulfate reducers, only one pure culture of a sulfate-reducing bacterium growing on DMS has been isolated from a thermophilic digestor [87]. The strain, which belongs to the genus *Desulfotomaculum*, oxidizes DMS to carbon dioxide forming 2.5 mol of sulfide per mole of DMS (table 4).

Denitrifying bacteria reduce nitrate or nitrite to NO, N_2O, and N_2 using a large variety of compounds including sugars, amino acids, alcohols, and organic acids. So far, only one pure culture of a denitrifier able to degrade DMS anaerobically with nitrate as electron acceptor has been

Table 7. Comparison of the main characteristics of DMS-degrading anaerobic microorganisms and some closely related (non-DMS-degrading) methanogens.

Name (type strain)	Origin	Substrate	pH[a]	Temperature (°C)[a]	NaCl (M)[a]	16S rRNA sequence[b]	Reference
DMS degrading methanogens							
Ml. taylorii (GS-16T)	Francisco Bay, Oregon, USA (E)	Me, Ma, MeS	8.0 (6.0–9.0)	29–37 (4–40)	0.5 (0.2–1.4)	U20154	[54, 110, 111]
Ml. bombayensis (B-1^T)	Arabian Sea, Bombay, India (M)	Me, Ma, MeS	7.2 (6.0–8.5)	37 (20–40)	0.5 (0.25–2.0)	U20148	[112]
Ml. oregonensis (WAL1^T)	Alkali Lake, Oregon, USA (ASL)	Me, Ma, MeS	8.1–9.1 (7.6–9.4)	35–37 (20–40)	< 0.5 (0.1–1.5)	U20152	[113]
Ms. siciliae (T4/M^T)	Sicily, Italy (M)	Me, Ma, MeS	6.5–6.8 (5.8–7.2)	37–40 (20–48)	0.4–0.6 (0.1–1.5)	U20153	[94, 114]
Ms. siciliae (HI350^T)	Oil well, Mexico (M)	Me, Ma, MeS	6.5–6.8 (5.8–7.2)	40 (20–48)	0.4–0.6 (0.1–1.5)	N.R.	[94]
Ms. siciliae (C2J^T)	Scripps Canyon, California, USA (M)	Me, Ma, MeS, Ac	6.0–7.0 (5.0–8.0)	35 (20–45)	0.2–0.6 (0–0.6)	U89773	[115]
Ms. acetivorans (C2A^T)	Scripps Canyon, California, USA (M)	Me, Ma, MeS, Ac	6.5–7.0 (5.5–8.0)	35–40 (15–45)	0.1–0.4 (< 1.0)	M59137	[116]
Ms. semesiae (MD1^T)	Mtoni Creek, Tanzania (MF)	Me, Ma, MeS	6.5–7.5 (6.2–8.3)	30–35 (18–39)	0.2–0.6 (N.R.)	AJ012742	[117]
Msa. zhilinaeae (WeN5^T)	Bosa Lake, Egypt (ASL)	Me, Ma, MeS	9.2 (8.2–10.3)	45 (N.R.)	0.7 (0.2–2.1)	–[c]	[118, 119]
Msa. zhilinaeae (Z-7936^T)	Lake Magadi, Kenya (SL)	Me, Ma, MeS	8.7–9.2 (7.8–10.2)	37 (20–48)	0.4 (0.2–2.2)	N.R.	[120]
Strain MTP4 (MTP4^T)	Bordeaux, France (SM)	Me, Ma, MeS, Ac	6.9–7.6 (6.1–8.0)	30 (12–35)	35–400 (35–400)	N.R.	[85]
Mm. hollandica (DMS1^T)	Dekkerswald, The Netherlands (F)	Me, Ma, MeS	6.5–7.0 (6.0–8.0)	34–37 (12–40)	0.04 (0–0.4)	AF120163	[91]
Closely related (non-DMS degrading) methanogens							
Mcc. burtonii (DSM 6242T)	Ace Lake, Antarctica (SL)	Me, Ma	7.7 (6.7–8.3)	23 (2–30)	0.2 (0.2–0.5)	X65537	[121]
Mcc. methylutens (TMA-10^T)	Scripps Canyon, California, USA (M)	Me, Ma	7.0–7.5 (6.0–8.0)	30–35 (15–35)	0.4 (0.2–1.0)	M59127	[122]
Mhl. halophilus (Z-7982^T)	Shark Bay, Australia (MCM)	Me, Ma	6.5–7.4 (6.3–8.0)	26–36 (18–40)	1.2–1.5 (0.3–2.6)	N.R.	[123]
Mhl. mahii (SLP^T)	Great Salt Lake, Utah, USA (SL)	Me, Ma	7.5 (6.5–8.5)	35 (<45)	2.0 (0.5–3.5)	M59133	[124, 125]
Ms. barkeri (MS^T)	Sewage digester, Illinois, USA (D)	H_2, Me, Ma, Ac	5.0–7.0 (4.0–8.0)	35–42 (20–50)	< 0.2 (<0.9)	AJ012094	[126, 127]

The origin of inoculum is given by the following symbols: ASL, alkaline salt lake sediment; D, anaerobic sewage digester; E, estuarine sediment; F, freshwater sediment; M, marine sediment; MCM, marine cyanobacterial mat; MF, mangrove forest sediment; SL, salt-lake sediment; SM, salt marsh sediment. The substrates for methanogenesis: Me, methanol; Ma, methylamines; MeS, methylated sulfur compounds; Ac, acetate. Abbreviations of taxa: *Mcc.*, *Methanococcoides*; *Mhl., Methanohalophilus*; *Ml., Methanolobus*; *Mm., Methanomethylovorans*; *Ms., Methanosarcina*; *Msa., Methanosalsus*. N.R. = not reported.

[a] Values given represent the optimum pH, temperature, and salt concentration for growth (ranges given within parentheses).

[b] Accession number for the GenBank/EMBL database except where mentioned otherwise.

[c] Sequence retrieved from Ribosomal Database Project (RDP: Mha.zhilin).

isolated from marine sediments [79]. This organism demethylates DMS, and the resulting methyl groups are further oxidized to carbon dioxide. Recently, DMS was observed to be completely degraded in nitrate-amended freshwater sediment slurries after a long period, but the responsible organism(s) was(were) not isolated [96].

Microbial conversions of VOSCs in situ

The relative importance in the cycling of VOSCs by the microbial mechanisms mentioned above depends on the ecosystem. As already mentioned, DMSP is the most important precursor for MT and DMS in marine and estuarine systems. Because of the complex community structures in these ecosystems, DMSP and other organic sulfur compounds are continuously interconverted. In this way, highly active mini-sulfur and carbon cycles are realized which are strongly influenced by environmental parameters like light intensity, temperature, pH, and the tidal movement of water. In contrast to many of saline habitats, freshwater systems are less dynamic, more organic rich, and poor in DMSP [97, 98]. In oligotrophic freshwater ecosystems, sulfide was found to be primarily converted to metal sulfides, especially FeS and FeS_2, whereas in eutrophic systems, sulfide was incorporated into the organic matter chemically and biologically (e. g. by sulfate reducers) [99]. Because of the higher organic matter content of many freshwater systems, mechanisms generating VOSCs from this organic matter, such as the methylation of sulfide or the production of VOSCs from sulfur-containing amino acids, are likely to be more important than formation from DMSP. Most of the data on sulfur compound cycling in freshwater systems is related to sulfide and sulfate, but little is known about the microbial cycling of VOSCs [60, 100–104]. Moreover, only a limited number of microorganisms that produce or degrade VOSCs have been isolated from these systems. No correlation was found between sulfate or chlorophyll concentration and the concentration of VOSCs in various freshwater lakes [103]. Depth VOSC profiles showed that in freshwater sediments, DMS was the main VOSC, whereas in marine sediments, mainly MT was detected. VOSC concentrations were highest in or just above the freshwater sediment, and both VOSC and H_2S concentrations decreased dramatically toward the water surface [60, 103]. The sediment was therefore concluded to be the major VOSC-producing compartment. The production and consumption of VOSCs in freshwater sediments appeared to be well balanced [60]. The ventilation of VOSCs to the atmosphere was found to be dramatically affected by the height of the water column on top of the sediment [101–104].

Since methanogens are considered as the major VOSC-degrading and – producing organisms in the anaerobic sediments of freshwater ecosystems [3, 4], this group of organisms and their metabolic properties will be discussed in more detail.

Methanogenic conversion of VOSCs

Methanogens are strict anaerobes that form methane as the end product of their energy metabolism. Phylogenetically, methanogens belong to the Archaea, which include several methanogenic lineages [105, 106]. The methanogens are characterized by a number of specific properties and a rather unique biochemistry [107, 108]. They exhibit an extreme habitat diversity and have been isolated from a large variety of anaerobic (micro)habitats including sediments of marine, estuarine, freshwater, and (salt) lake origin, digestive and intestinal tracts of animals and insects, anaerobic waste reactors, geothermal springs, and hydrothermal vents [109]. Methanogens as a group have a small substrate spectrum and different species generally only use one or two compounds [105, 109] (table 6). An exception is the genus *Methanosarcina*, whose members can metabolize the majority of methanogenic substrates, including methylated sulfur compounds. Since many of these compounds are products of the degradation of larger (macro)molecules, methanogens rely on the catabolic activity of other (micro)organisms in their environment for the continuous supply of their substrates. During the last 10 years, several methanogens have been isolated that are able to convert and grow on MT and DMS (table 7).

Although not studied in detail, methanogenesis from DMS and MT is likely to occur in a similar way to that of structural analogs like methanol and methylated amines, since all compounds are disproportionated to methane and carbon dioxide. Methanogenesis from methylated substrates requires methyl group abstraction and subsequent methylation of 2-mercaptoethanesulfonic acid (HS-CoM), followed by conversion of methyl-CoM to methane with reducing equivalents obtained from the concomitant oxidation of the methylotrophic substrate to carbon dioxide [107, 108]. Two different methyltransferases are involved in this reaction sequence: MT_1, a corrinoid-containing enzyme which accepts the methyl group from the substrate, and MT_2, which transfers the enzyme-bound methyl group to HS-CoM. MT_1 only accepts a methyl group when the corrinoid is present in its fully reduced Co(I) state. Activation of Co(II) or Co(III) MT_1 occurs by reductive activation (fig. 6) [128, 129]. During growth on different substrates, MT_1 and MT_2 isozymes with different substrate specificities are produced [125–128]. In the final step of methanogenesis, methyl-CoM is reduced by 7-mercaptoheptanoylthreonine phosphate (HS-HTP) to methane, and the heterodisulfide of HS-CoM and HS-HTP (CoM-S-S-HTP)

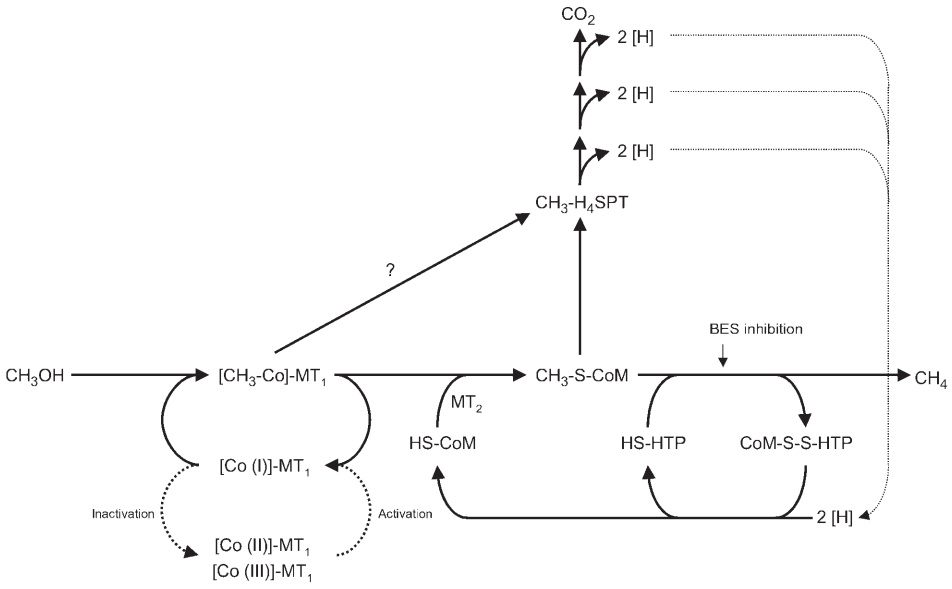

Figure 6. Mechanism for methanogenic degradation of methylated compounds based on that of methanol degradation by *Methanosarcina barkeri* [130–135]. H_4SPT, 5,6,7,8-tetrahydrosarcinapterin; HS-CoM, coenzyme M; HS-HTP, 7-mercaptoheptanoylthreonine phosphate; MT_1, methanol: 5-hydroxybenzimidazolylcobamide methyltransferase; MT_2, Co methyl-5-hydroxy-benzimidazolylcobamide:coenzyme M methyltransferase.Question mark indicates a reaction that has not yet been elucidated.

by methylcoenzyme M reductase. The heterodisulfide is then reduced by the membrane-bound enzyme heterodisulfide reductase to recover HS-CoM and HS-HTP (fig. 6). In this reduction step, energy is conserved by the translocation of protons over the cell membrane [107, 108]. Compared to methanol, the biochemical pathway for the conversion of methylated sulfur compounds is poorly understood. Since cell extracts of methylotrophic methanogens grown on methanol or trimethylamine were unable to convert DMS or MT, these substrates are most likely converted by distinct inducible enzymes [93]. Crude extracts of *Methanosarcina barkeri* strain MS, prepared from acetate-grown cells, were recently found to be able to convert DMS to methane. The responsible HS-CoM methylating enzyme contained a bound corrinoid [134].

In some cases, methylated compounds can also be completely oxidized by methanogens to carbon dioxide. In this case, the reducing equivalents formed (hydrogen) must be removed by hydrogenotrophic microorganisms like denitrifiers or sulfate/sulfite reducers. This process is called interspecies hydrogen transfer [135].

In complex systems like sediment slurries, selective inhibition of specific microbes can be very helpful to elucidate the metabolic flux of certain compounds. Bromoethanesulfonic acid (BES) is a structural analog of HS-CoM and is a competitive inhibitor of methylcoenzyme M reductase [136]. Since HS-CoM and methylcoenzyme M reductase are present in all methanogens and only a few other microorganisms (some methylotrophs and *Xanthobacter* species), BES acts as a relatively specific inhibitor. Moreover, BES inhibition is independent of the substrate for methanogenesis due to the crucial role of methylcoenzyme M reductase in the methanogenic pathway. In general, inhibition will be immediate, but in some cases, lag phases up to 48 h were needed to obtain complete inhibition [137]. The concentrations of BES required to obtain complete inhibition of methanogenic bacteria differs strongly, and is generally higher for environmental samples than for pure cultures of methanogens [138; B. P. Lomans unpublished results].

Conclusions

Anaerobic methylation of sulfide and MT, and methanogenic conversion of MT and DMS are the dominant processes in anaerobic cycling of these VOSCs in freshwater habitats (fig. 7). MT and DMS are mainly formed in the sediment. The balance between these processes results in an anaerobic mineralization of methyl groups. First, sulfide (or MT) receives a methyl group from methoxylated aromatic compounds (like syringate and 3,4,5-trimethoxybenzoate) resulting in formation of MT or DMS. The methylated sulfur compounds in turn are converted by methanogens leading to recycling of sulfide and production of methane. Several factors that may affect this balance, resulting in higher or lower fluxes of MT and DMS to the atmosphere, have been identified. VOSC formation was found to be stimulated by sulfide (in equilibrium with H_2S), sulfate (indirectly), and methyl-group-donating compounds, and

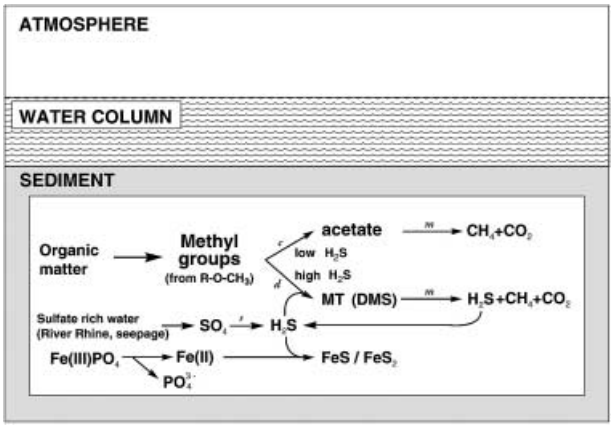

Figure 7. Cycling of VOSC in anoxic freshwater sediments. Formation of acetate from methyl groups occurs under conditions of low sulfide concentrations through carbonylation (*c*). Formation of MT and DMS occurs only under conditions of high sulfide concentrations since sulfide is required as methyl group acceptor (*d*). Sulfide acting as methyl group acceptor to form MT and subsequently DMS is generated in the system by sulfate reduction (*s*), decomposition of organic matter, and degradation of MT and DMS by methanogenic activity (*m*). Sulfate can be introduced in the system by several processes (inlet of sulfate-rich river water, deposition, and seepage water). MT, DMS, and H_2S can be restored or converted in the sediment, or diffuse to the higher aerobic water column and atmosphere.

was inhibited by free iron. The latter compound results in precipitation of iron sulfides (fig. 7). VOSC degradation by *M. hollandica* was found to be inhibited by sulfide [91]. Furthermore, the presence of sulfate in the sediments was found to stimulate VOSC degradation by sulfate-reducing bacteria. These findings are very important from the ecological point of view since increased sulfate concentrations in several freshwater ecosystems caused by the inlet of river water [139] (with the river Rhine as a good example) into these systems have resulted in higher H_2S concentrations in systems which were iron limited. These higher sulfate and H_2S concentrations are likely to enhance VOSC formation through sulfide methylation, and VOSC degradation by sulfate-reducing bacteria, whereas VOSC degradation by methanogens is likely to be inhibited. Although more research is needed to be able to predict the outcome of the combination of these processes, higher fluxes of VOSCs from sulfide-rich systems toward the atmosphere are conceivable.

1 Kelly D. P. and Baker S. C. (1991) The organosulphur cycle: aerobic and anaerobic processes leading to the turnover of C_1 compounds. FEMS Microbiol. Rev. **87:** 241–246
2 Kelly D. P. and Smith N. A. (1991) Organic sulfur compounds in the environment: biochemistry, microbiology and ecological aspects. Adv. Microb. Ecol. **11:** 345–385
3 Zinder S. H. and Brock T. D. (1978) Methane, carbon dioxide, and hydrogen sulfide production from the terminal methiol group of methionine by anaerobic lake sediments. Appl. Environ. Microbiol. **35:** 344–352
4 Zinder S. H. and Brock T. D. (1978) Production of methane and carbon dioxide from methane thiol and dimethyl sulfide by anaerobic lake sediments. Nature **273:** 226–228
5 Middelburg J. J. (2000) The geochemical sulfur cycle. In: Environmental Technologies to Treat Sulfur Pollution: Principles and Engineering, pp. 33–46, Lens P. and Hulshoff Pol L. (eds), IWA, London
6 Lovelock J. E., Maggs R. J. and Rasmussen R. A. (1972) Atmospheric dimethyl sulfide and the natural sulfur cycle. Nature **237:** 452–453
7 Bremner J. M. and Steele C. G. (1978) Role of microorganisms in the atmospheric sulfur cycle. Adv. Microb. Ecol. **2:** 155–201
8 Charlson R. J., Lovelock J. E., Andreae M. O. and Warren S. G. (1987) Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. Nature **326:** 655–661
9 Verschueren K. (1983) Handbook of environmental data on organic chemicals, 2nd edn, Van Nostrand Reinhold, New York
10 Derikx P. J. L., Op den Camp H. J. M., Drift C. van der, Van Griensven L. J. L. D. and Vogels G. D. (1991) Odorous sulfur compounds emitted during production of compost used as a substrate in mushroom cultivation. Appl. Environ. Microbiol. **56:** 176–180
11 Bhatia S. P. (1978) Organosulfur emissions from industrial sources. In: Sulfur in the Environment, pp. 51–83, Nriagu J. O. (ed.), Wiley, New York
12 Suylen G. M. H. (1988) Microbial Metabolism of Dimethyl Sulphide and Related Compounds. Ph.D. thesis, University of Technology, Delft, The Netherlands
13 Merck Index (1989) 11th edn, Merck, Rahway
14 König W. A., Ludwig K., Sievers L., Rinken M., Stölting K. H. and Günther W. (1980) Identification of volatile organic sulfur compounds in municipal sewage systems by GC/MS. J. High Resolut. Chromatogr. Chromatogr. Commun. **3:** 415–416
15 Sivelä S. and Sundmann V. (1975) Demonstration of *Thiobacillus*-type bacteria, which utilize methyl sulphides. Arch. Microbiol. **103:** 303–304
16 Kiene R. P. and Bates T. S. (1991) Biological removal of dimethyl sulfide from sea water. Nature **345:** 702–705
17 Ferchichi M., Hemme D. and Nardi M. (1986). Induction of methanethiol production by *Brevibacterium linens* CNRZ 918. J. Gen. Microbiol. **132:** 3075–3082
18 Kadota H. and Ishida Y. (1972) Production of volatile sulfur compounds by microorganisms. Annu. Rev. Microbiol. **26:** 127–138
19 Kiene R. P. and Visscher P. T. (1987) Production and fate of methylated sulfur compounds from methionine and dimethylsulfoniopropionate in salt marsh sediments. Appl. Environ. Microbiol. **53:** 2426–2434
20 Segal W. and Starkey R. L. (1969) Microbial decomposition of methionine and identity of resulting sulfur compounds. J. Bacteriol. **98:** 908–913
21 Kiene R. P. and Capone D. G. (1988) Microbial transformations of methylated sulfur compounds in anoxic salt marsh sediments. Microb. Ecol. **15:** 275–291
22 Dacey J. W. H. and Blough N. V. (1987) Hydroxide decomposition of dimethylsulfoniopropionate to form dimethyl sulfide. Geophys. Res. Lett. **14:** 1246–1249
23 Dickson D. M., Wyn Jones R. G. and Davenport J. (1980) Steady state osmotic adaptation in *Ulva lactuca*. Planta **150:** 158–164
24 Turner S. M., Malin G. and Liss P. S. (1988) The seasonal variation of dimethyl sulfide and dimethylsulfoniopropionate concentrations in nearshore waters. Limnol. Oceanogr. **33:** 364–375
25 Vairavamurthy A., Andreae M. O. and Iverson R. L. (1985) Biosynthesis of dimethyl sulfide and dimethylpropiothetin by

Hymenomonas carterae in relation to sulfur source and salinity variations. Limnol. Oceanogr. **30:** 59–70
26 Kiene R. P. (1990) Dimethyl sulfide production from dimethylsulfoniopropionate in coastal seawater and bacterial cultures. Appl. Environ. Microbiol. **56:** 3292–3297
27 De Souza M. P. and Yoch D. C. (1995) Comparative physiology of dimethyl sulfide production by dimethylsulfoniopropionate lyase in *Pseudomonas doudoroffii* and *Alcaligenes* sp. strain M3A. Appl. Environ. Microbiol. **61:** 3986–3991
28 Diaz M. R., Visscher P. T. and Taylor B. F. (1992) Metabolism of dimthylsulfoniopropionate and glycine betaine by a marine bacterium. FEMS Microbiol. Lett. **96:** 61–66
29 Wagner C. and Stadtmann E. R. (1962) Bacterial fermentation of dimethyl-β-propiothetin. Arch. Biochem. Biophys. **98:** 331–336
30 Van der Maarel M. J. E. C. and Hansen T. A. (1996) Anaerobic microorganisms involved in the degradation of DMS(P). In: Biological and Environmental Chemistry of DMSP and Related Sulfonium Compounds, pp. 351–360, Kiene R. P., Visscher P. T., Keller M. D. and Kirst G. O. (eds), Plenum, New York
31 Ansede J. H., Friedman R. and Yoch D. C. (2001) Phylogenetic analysis of culturable dimethyl sulfide-producing bacteria from a *Spartina*-dominated salt marsh and estuarine water. Appl. Environ. Microbiol. **67:** 1210–1217
32 Niki T., Kunugi M. and Otsuki A. (2000) DMSP-lyase activity in five marine phytoplankton species: its potential importance in DMS production. Mar. Biol. **136:** 759–764
33 Tang K. W., Visscher P. T. and Dam H. G. (2001) DMSP-consuming bacteria associated with the calanoid copepod *Acartia tonsa* (Dana). J. Exp. Mar. Biol. Ecol. **256:** 185–198
34 Zubkov M. V., Fuchs B. M., Archer S. D., Kiene R. P., Amann R. and Burkill P. H. (2001) Linking the composition of bacterioplankton to rapid turnover of dissolved dimethylsulphoniopropionate in an algal bloom in the North Sea. Environ. Microbiol. **3:** 304–311
35 Dacey J. W. H. and Wakeham S. G. (1986) Oceanic dimethyl sulfide: production during zooplankton grazing on phytoplankton. Science **233:** 1314–1316
36 Ishida Y. (1968) Physiological studies on evolution of dimethyl sulfide from unicellular marine algae. Mem. Coll. Agric. Kyoto. Univ. **94:** 47–82
37 Iverson R. L., Nearhoof F. L. and Andreae M. O. (1989) Production of dimethylsulfonium propionate and dimethylsulfide by phytoplankton in estuarine and coastal waters. Limnol. Oceanogr. **34:** 53–67
38 Kadota H. and Ishida Y. (1968) Effects of salts on enzymatical production of dimethyl sulfide from *Gyrodinium cohnii*. Bull. Jpn Soc. Sci. Fish. **34:** 512–518
39 Stefels J. and Boekel W. H. M. van (1993) Production of DMS from dissolved DMSP in axenic cultures of the marine phytoplankton species *Phaeocystis* sp. Mar. Ecol. Prog. Ser. **97:** 11–18
40 Hanson A. D. and Gage D. A. (1996) Dimethylsulfoniopropionate biosynthesis and use by flowering plants. In: Biological and Environmental Chemistry of Dimethylsulfoniopropionate and Related Sulfonium Compounds, pp. 75–86, Kiene R. P., Visscher P. T., Keller M. D. and Kirst G. O. (eds), Plenum, New York
41 Bacic M. K. and Yoch D. C. (1998) In vivo characterization of dimethylsulfoniopropionate lyase in the fungus *Fusarium lateritium*. Appl. Environ. Microbiol. **64:** 106–111
42 Kiene R. P. and Taylor B. F. (1988) Demethylation of dimethylsulfoniopropionate and production of thiols in anoxic marine sediments. Appl. Environ. Microbiol. **54:** 2208–2212
43 Kiene R. P. and Taylor B. F. (1988) Biotransformation of organosulfur compounds in sediments via 3-mercaptopropionate. Nature **332:** 148–150
44 Taylor B. F. and Gilchrist D. C. (1991) New routes for aerobic degradation of dimethylsulfoniopropionate. Appl. Environ. Microbiol. **57:** 3581–3584
45 Taylor B. F. and Visscher P. T. (1996) Metabolic pathways involved in DMSP degradation. In: Environmental and Biological Chemistry of Dimethylsulfoniopropionate and Related Sulfonium Compounds, pp. 265–276, Kiene R. P., Visscher P. T., Keller M. D. and Kirst G. O. (eds), Plenum, New York
46 Van der Maarel M. J. E. C., Jansen M., Haanstra R., Meijer W. G. and Hansen T. A. (1996) Demethylation of dimethylsulfoniopropionate to 3-S-methylmercaptopropionate by marine sulfate-reducing bacteria. Appl. Environ. Microbiol. **62:** 3978–3984
47 Van der Maarel M. J. E. C., Quist P., Dijkhuizen L. and Hansen T. A. (1993) Degradation of dimethylsulfoniopropionate to 3-S-methylmercaptopropionate by a marine *Desulfobacterium* strain. Arch. Microbiol. **60:** 411–412
48 Visscher P. T. and Taylor B. F. (1994) Demethylation of dimethylsulfoniopropionate to 3-mercaptopropionate by an aerobic marine bacterium. Appl. Environ. Microbiol. **60:** 4617–4619
49 Van der Maarel M. J. E. C., Jansen M. and Hansen T. A. (1995) Methanogenic conversion of 3-S-methylmercaptopropionate to 3-mercaptopropionate. Appl. Environ. Microbiol. **61:** 48–51
50 Andreae M. O. (1980) Dimethylsulfoxide in marine and freshwaters. Limnol. Oceanogr. **25:** 1054–1063
51 Distefano V. and Borgstedt H. (1964) Reduction of dimethylsulfoxide to dimethyl sulfide in the cat. Science **144:** 1137–1138
52 Griebler C. (1997) Dimethylsulfoxide (DMSO) reduction: a new approach to determine microbial activity in freshwater sediments. J. Microbiol. Methods **29:** 31–40
53 Zinder S. H. and Brock T. D. (1978) Dimethyl sulfoxide as an electron acceptor for anaerobic growth. Arch. Microbiol. **116:** 35–40
54 Kiene R. P., Orenland R. S., Catena A., Miller L. G. and Capone D. G. (1986). Metabolism of reduced methylated sulfur compounds in anaerobic sediments and by a pure culture of an estuarine methanogen. Appl. Environ. Microbiol. **52:** 1037–1045
55 Drotar A., Burton G. A. Jr and Tavernier J. E. (1987) Widespread occurrence of bacterial thiol methyltransferases and the biogenic emission of methylated sulfur gases. Appl. Environ. Microbiol. **53:** 1626–1631
56 Larsen G. L. (1985) Distribution of cysteine conjugate β-lyase in gastrointestinal bacteria and in the environment. Xenobiotica **15:** 199–210
57 Bak F., Finster K. and Rothfuss F. (1992) Formation of dimethyl sulfide and methanethiol from methoxylated aromatic compounds and inorganic sulfide by newly isolated anaerobic bacteria. Arch. Microbiol. **157:** 529–534
58 Finster K., King G. M. and Bak F. (1990) Formation of methyl mercaptan and dimethyl sulfide from methoxylated aromatic compounds in anoxic marine and freshwater sediments. FEMS Microbiol. Ecol. **74:** 295–302
59 Kiene R. P., and Hines M. E. (1995) Microbial formation of dimethyl sulfide in anoxic *Sphagnum* peat. Appl. Environ. Microbiol. **61:** 2720–2726
60 Lomans B. P., Smolders A. J. P., Intven L. M., Pol A., Op den Camp H. J. M. and Drift C. van der (1997) Formation of dimethyl sulfide and methanethiol in anoxic freshwater sediments. Appl. Environ. Microbiol. **63:** 4741–4747
61 Bache R. and Pfennig N. (1981) Selective isolation of *Acetobacterium woodii* on methoxylated aromatic acids and determination of growth yields. Arch. Microbiol. **130:** 255–261
62 Stupperich E. and Konle R. (1993) Corrinoid-dependent methyl transfer reactions are involved in methanol and

3,4-dimethoxybenzoate metabolism by *Sporomusa ovata*. Appl. Environ. Microbiol. **59:** 3110–3116
63 Daniel S. L., Keith E. S., Yang H. C., Lin Y. S. and Drake H. L. (1991) Utilization of methoxylated aromatic compounds by the acetogen *Clostridium thermoaceticum*: expression and specificity of the CO-dependent *O*-demethylating activity. Biochem. Biophys. Res. Commun. **180:** 416–422
64 Liu S. and Suflita J. M. (1993) H_2-CO_2-dependent anaerobic *O*-demethylation activity in subsurface sediments by an isolated bacterium. Appl. Environ. Microbiol. **59:** 1325–1331
65 Grech-Mora I., Fardeau M.-L., Patel B. K. C., Ollivier B., Rimbault A., Prensier G. et al. (1996) Isolation and characterization of *Sporobacter termitidis* gen. nov., sp. nov., from the digestive tract of the wood-feeding termite *Nasutitermes lujae*. Int. J. Syst. Bacteriol. **46:** 512–518
66 Mechichi T., Labat M, Garcia J.-L., Thomas P. and Patel B. K. C. (1999) *Sporobacterium olearium* gen. nov., sp. nov., a new methanethiol-producing bacterium that degrades aromatic compounds, isolated from an olive mill wastewaster treatment digester. Int. J. Syst. Bacteriol. **49:** 1741–1748
67 Lomans B. P., Leijdekkers P., Wesselink J. J., Bakkes P., Pol A., Drift C. van der et al. (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. Appl. Environ. Microbiol. **67:** 4017–4023
68 Mechichi T., Labat M., Patel B. K. C., Woo T. H. S., Thomas P. and Garcia J.-L. (1999) *Clostridium methoxybenzovorans* sp. nov., a new aromatic *O*-demethylating homoacetogen from an olive mill waste treatment digester. Int. J. Syst. Bacteriol. **49:** 1201–1209
69 Kreft J.-U. and Schink B. (1993) Demethylation and degradation of phenylmethylethers by the sulfide-methylating homoacotogenic bacterium strain TMBS 4. Arch. Microbiol. **159:** 308–315
70 Kreft J.-U. (1995) The Methyl Ester Cleaving Enzyme System of the Anaerobic Bacterium *Holophaga foetida*. Ph.D. thesis, Universität Konstanz, Germany
71 Hatakka A. (1994) Lignin-modifying enzymes from selected white-rot fungi: production and role in lignin degradation. FEMS Microbiol. Rev. **13:** 125–134
72 De Zwart J. M. M. and Kuenen J. G. (1997) Aerobic conversion of dimethyl sulfide and hydrogen sulfide by *Methylophaga sulfidovorans*: implications for modeling DMS conversion in a microbial mat. FEMS Microbiol. Ecol. **22:** 155–165
73 Cho K., Hirai M. and Shoda M. (1991) Degradation characteristics of hydrogen sulfide, methanethiol, dimethyl sulfide and dimethyl disulfide by *Thiobacillus thioparus* DW44 isolated from peat biofilter. J. Ferm. Bioeng. **71:** 384–389
74 Cho K., Zhang L., Hirai M. and Shoda M. (1991) Removal characteristics of hydrogen sulfide and methanethiol by *Thiobacillus* sp. isolated from peat in biological deodorization. J. Ferm. Bioeng. **71:** 44–49
75 De Bont J. A. M., Dijken J. P. van and Harder W. (1981) Dimethyl sulphoxide and dimethyl sulphide as a carbon, sulphur and energy source for growth of *Hyphomicrobium* S. J. Gen. Microbiol. **127:** 315–323
76 De Zwart J. M. M., Nelisse P. N. and Kuenen J. G. (1996) Isolation and characterization of *Methylophaga sulfidovorans* sp. nov.: an obligate methylotrophic aerobic, DMS oxidizing bacterium from a microbial mat. FEMS Microbiol. Ecol. **20:** 261–271
77 Pol A., Op den Camp H. J. M., Mees S. G. M., Kersten M. A. S. H. and Drift C. van der (1994) Isolation of a dimethyl sulfide utilizing *Hyphomicrobium* species and its application in biofiltration of polluted air. Biodegradation **5:** 105–112
78 Smith N. A. and Kelly D. P. (1988) Isolation and physiological characterization of autotrophic sulphur bacteria oxidizing dimethyl disulphide as sole source of energy. J. Gen. Microbiol **134:** 1407–1417
79 Visscher P. T. and Taylor B. F. (1993) A new mechanism for the aerobic catabolism of dimethyl sulfide. Appl. Environ. Microbiol. **59:** 3784–3789
80 Visscher P. T., Quist P. and Gemerden H. van (1991) Methylated sulfur compounds in microbial mats: in situ concentrations and metabolism by a colorless sulfur bacterium. Appl. Environ. Microbiol. **57:** 1758–1763
81 Zhang L., Hirai M. and Shoda M. (1991) Removal characteristics of dimethyl sulfide, methanethiol and hydrogen sulfide by *Hyphomicrobium* sp. 155 isolated from peat biofilter. J. Ferm. Bioeng. **5:** 392–396
82 Zhang L., Kuniyoshi I., Hirai M. and Shoda M. (1991) Oxidation of dimethyl sulfide by *Pseudomonas acidovorans* DMR-11 isolated from peat biofilter. Biotech. Lett. **13:** 223–228
83 Holland H. L. (1988) Chiral sulfoxidation by biotransformations of organic sulfides. Chem. Rev. **88:** 473–485
84 Neidleman S. L. and Geigert J. (1986). Biohalogenation: Principles, Basic Roles and Aplications. Horwood, Chichester
85 Finster K., Tanimoto Y. and Bak F. (1992) Fermentation of methanethiol and dimethylsulfide by a newly isolated methanogenic bacterium. Arch. Microbiol. **157:** 425–430
86 Kiene R. P. (1988) Dimethyl sulfide metabolism in salt marsh sediments. FEMS Microb. Ecol. **53:** 71–78
87 Tanimoto Y., and Bak F. (1994) Anaerobic degradation of methyl mercaptan and dimethyl sulfide by newly isolated sulfate reducing bacteria. Appl. Environ. Microbiol. **60:** 2450–2455
88 Visscher P. T., and Gemerden H. van (1991) Photoautotrophic growth of *Thiocapsa roseopersicina* on dimethyl sulfide. FEMS Microbiol. Lett. **81:** 247–250
89 Zeyer J., Eicher P., Wakeham S. G. and Schwarzenbach R. P. (1987) Oxidation of dimethyl sulfide to dimethylsulfoxide by phototrophic purple bacteria. Appl. Environ. Microbiol. **53:** 2026–2032
90 Rajagopal B. S. and Daniels L. (1986). Investigations of mercaptans, organic sulfides, and inorganic sulfur sources for the growth of methanogenic bacteria. Curr. Microbiol. **14:** 137–144
91 Lomans B. P., Maas R., Luderer R., Op den Camp H. M. J., Pol A., Drift C. van der et al. (1999) 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. Appl. Environ Microbiol. **65:** 3641–3650
92 Lomans B. P., Luderer R., Steenbakkers P., Pol A., Drift C. van der, Vogels G. D. et al. (2001) Microbial populations involved in cycling of dimethyl sulfide and methanethiol in freshwater sediments. Appl. Environ. Microbiol. **67:** 1044–1051
93 Ni S. and Boone D. R. (1993) Catabolism of dimethyl sulfide and methanethiol by methylotrophic methanogens. In: Biogeochemistry of Global Change, pp. 796–810, Oremland R. S. (ed.), Chapman & Hall, New York
94 Ni S. and Boone D. R. (1991) Isolation and characterisation of a dimethyl sulfide degrading methanogen, *Methanolobus siciliae* HI350, from an oil well, characterisation of *M. siciliae* $T4/M^T$ and emendation of *M. siciliae*. Int. J. Syst. Bacteriol. **41:** 410–416
95 Jones J. G., Simon B. M. and Gardener S. (1982) Factors affecting methanogenesis and associated anaerobic processes in the sediments of a stratified eutrophic lake. J. Gen. Microbiol. **128:** 1–11
96 Lomans B. P., Op den Camp H. J. M., Pol A., Drift C. van der and Vogels G. D. (1999) The role of methanogens and other bacteria in the degradation of dimethyl sulfide and methanethiol in anoxic freshwater sediments. Appl. Environ. Microbiol. **65:** 2116–2121

97 Challenger F., Bywood R., Thomas R. and Haywood B. J. (1957) Studies on biological methylation: the natural occurrence and chemical reactions of some thetins. Arch. Biochem. Biophys. **69:** 514–523

98 Bechard M. J. and Rayburn W. R. (1979) Volatile organic sulfides from freshwater algae. J. Phycol. **15:** 379–383

99 Rudd W. M., Kelly C. A. and Furutani A. (1986). The role of sulfate reduction in long term accumulation of organic and inorganic sulfur in lake sediments. Limnol. Oceanogr. **31:** 1281–1291

100 De Mello W. Z. and Hines M. E. (1994) Application of static and dynamic enclosures for determining dimethylsulfide and carbonyl sulfide exchange in *Sphagnum* peatlands: implications for the magnitude and direction of flux. J. Geophys. Res. D. Atmos. **99:** 14601–14607

101 Henatsch J. J. and Jüttner F. (1988) Capillary gas chromatographic analysis of low-boiling organic sulphur compounds in anoxic lake-water by cryo-adsorption. J. Chromatogr. **445:** 97–105

102 Henatsch J. J. and Jüttner F. (1991) Occurrence and distribution of methane thiol and other volatile organic sulphur compounds in a stratified lake with anoxic hypolimnion. Arch. Hydrobiol. **119:** 315–323

103 Richards S. R., Kelly C. A. and Rudd J. W. H. (1991) Organic volatile sulfur in lakes of the Canadian Shield and its loss to the atmosphere. Limnol. Oceanogr. **36:** 468–482

104 Richards S. R., Rudd J. W. M. and Kelly C. A. (1994) Organic volatile sulfur in lakes ranging in sulfate and dissolved salt concentration over five orders of magnitude. Limnol. Oceanogr. **39:** 562–572

105 Boone D. R., Whitman W. B. and Rouvière P. (1993) Diversity and taxonomy of methanogens. In: Methanogenesis, pp. 35–80, Ferry J. G. (ed.), Chapman & Hall, New York

106 Garcia J.-L., Patel B. K. C. and Ollivier B. (2000) Taxonomic, phylogenetic and ecological diversity of methanogenic Archaea. Anaerobe **6:** 205–226

107 Ferry J. G. (1999) Enzymology of one-carbon metabolism in methanogenic pathwways. FEMS Microbiol. Rev. **23:** 13–38

108 Thauer R. K. (1998) Biochemistry of methanogens. Microbiology **144:** 2377–2406

109 Zinder S. H. (1993) Physiological ecology of methanogens. In: Methanogenesis, pp. 128–206, Ferry J. G. (ed.), Chapman & Hall, New York

110 Oremland R. S. and Boone D. R. (1994) *Methanolobus taylorii* sp. nov., a new methylotrophic estuarine methanogen. Int. J. Syst. Bacteriol. **44:** 573–575

111 Oremland R. S., Kiene R. P., Whiticar M. J. and Boone D. R. (1989) Description of an estuarine methylotrophic methanogen which grows on dimethylsulfide. Appl. Environ. Microbiol. **55:** 994–1002

112 Kadam P. C., Ranade D. R., Mandelco L. and Boone D. R. (1994) Isolation and characterization of *Methanolobus bombayenis* sp. nov., a methylotrophic methanogen that requires high concentrations of divalent cations. Int. J. Syst. Bacteriol. **44:** 603–607

113 Liu Y., Boone D. R. and Choy C. (1991) *Methanohalophilus oregonense*, sp. nov., a methylotrophic methanogen from an alkaline, saline aquifer. Int. J. Syst. Bacteriol. **40:** 111–116

114 Stetter K. O. (1989) Genus II. *Methanolobus* König and Stetter 1983, 439^{VP}. In: Bergey's Manual of Systematic bacteriology, vol. 3, pp. 2205–2207, Staley J. T., Bryant M. P., Pfennig N. and Holt H. G. (eds), William & Wilkins, Baltimore

115 Elberson M. A. and Sowers K. R. (1997) Isolation of an aceticlastic strain of *Methanosarcina siciliae* from marine canyon sediments and emendation of the species describtion for *Methanosarcina siciliae*. Int. J. Syst. Bacteriol. **47:** 1258–1261

116 Sowers K. R., Baron S. F. and Ferry J. G. (1984) *Methanosarcina acetivorans* sp. nov., an acetotrophic methane-producing bacterium isolated from marine sediments. Appl. Environ. Miocrobiol. **47:** 971–978

117 Lyimo T. J., Pol A., Op den Camp H. J. M., Harhangi H. R. and Vogels G. D. (1998) Isolation and characterization of a dimethylsulfide-utilizing methanogen, *Methanosarcina semesiae* sp. nov., from mangrove sediment. Int. J. Syst. Evol. Bact. **50:** 171–178

118 Boone D. R., Worakit S., Mathrani I. M. and Mah R. A. (1986) Alkaliphilic methanogens from high-pH lake sediments. Syst. Appl. Microbiol. **7:** 230–234

119 Mathrani I. M., Boone D. R., Mah R. A., Fox G. E. and Lau P. P. (1988) *Methanohalophilus zhilinae* sp. nov., an alkaliphilic, halophilic, methylotrophic methanogen. Int. J. Syst. Bacteriol. **38:** 139–142

120 Kevbrin V. V., Lysenko A. M. and Zhilina T. N. (1997) Physiology of the alkaliphilic methanogen Z-7936, a new strain of *Methanosalsus zhilinaeae* isolated from Lake Magadi. Microbiologiya **66:** 261–266

121 Franzmann P. D., Springer N., Ludwig W., Conway de Macario E. and Rohde M. (1992) A methanogenic archaeon from Ace Lake, Antartica: *Methanococcoides burtonii* sp. nov.. Syst. Appl. Microbiol. **15:** 73–581

122 Sowers K. R. and Ferry J. G. (1985) Isolation and charaterization of a methylotrophic marine methanogen, *Methanococcoides methylutens* gen. nov., sp. nov. Appl. Environ. Microbiol. **45:** 684–690

123 Zhilina T. N. (1983) New obligate halophilic methane-producing bacterium. Microbiologiya **52:** 375–382

124 Paterek J. R. and Smith P. H. (1985) Isolation and characterization of a halophilic methanogen from Great Salt Lake. Appl. Environ. Microbiol. **50:** 877–881

125 Paterek J. R. and Smith P. H. (1988) *Methanohalophilus mahii* gen. nov., sp. nov., a methylotrophic halophilic methanogen. Int. J. Syst. Bacteriol. **38:** 122–123

126 Bryant M. P. and Boone D. R. (1987) Emended description of strain MS^T (DSM 800^T), the type strain of *Methanosarcina barkeri*. Int. J. Syst. Bacteriol. **37:** 169–170

127 Schnellen C. G. T. P. (1947) Research on Methane Fermentation (in Dutch) Ph. D. thesis, University of Technology, Delft, The Netherlands

128 Van der Meijden P., Heythuysen H. J., Pouwels A., Houwen F., Drift C. van der and Vogels G. D. (1983) Methyltransferases involved in methanol conversion by *Methanosarcina barkeri*. Arch. Microbiol. **134:** 238–242

129 Van der Meijden P., Lest C. van der, Drift C. van der and Vogels G. D. (1984) Reductive activation of methanol: 5-hydroxybenzimidazolyl-cobamide methyltransferase of *Methanosarcina barkeri*. Biochem. Biophys. Res. Commun. **118:** 760–766

130 Daas P. J. H. (1996) Methanol-Dependent Methyl Transfer Reactions in *Methanosarcina barkeri*. Ph.D. thesis, University of Nijmegen, The Netherlands

131 Grahame D. A. (1989) Different isozymes of methylcobalamin:2-mercaptoethanesulfonate methyltransferase predominate in methanol- versus acetate-grown *Methanosarcina barkeri*. J. Biol. Chem. **264:** 12890–12894

132 Wassenaar R. (1999) Methanogenesis from methylamines in *Methanosarcina barkeri* Fusaro. Ph.D. thesis, University of Nijmegen, The Netherlands

133 Yeliseev A., Gärtner P., Harms U., Linder D., Thauer R. K. (1993) Function of methylcobalamin:coenzyme M methyltransferase isoenzyme II in *Methanosarcina barkeri*. Arch. Microbiol. **159:** 530–536

134 Tallant T. C. and Krzycki J. A. (1997) Methylthiol:coenzyme M methyltransferase from *Methanosarcina barkeri*, an enzyme of methanogenesis from dimethyl sulfide and methylmercaptopropionate. J. Bacteriol. **179:** 6902–6911

135 Phelps T. J., Conrad R. and Zeikus J. G. (1985) Sulfate-dependent interspecies H_2 transfer between *Methanosarcina barkeri* and *Desulfovibrio vulgaris* during co-culture metabolism on acetate or methanol. Appl. Environ. Microbiol. **50:** 589–594

136 Gunsalus R. P. and Wolfe R. S. (1978) ATP activation and properties of the methyl coenzyme M reductase system in *Methanobacterium thermoautotrophicum*. J. Bacteriol. **135:** 851–857

137 King G. M., Klug M. J. and Lovely D. R. (1983) Metabolism of acetate, methanol and methylated amines in intertidal sediments of Lowes Cove, Maine. Appl. Environ. Microbiol. **45:** 1848–1853

138 Oremland R. S. and Capone D. G. (1988) Use of 'specific' inhibitors in biogeochemistry and microbial ecology. Adv. Microb. Ecol. **10:** 285–383

139 Roelofs J. G. M. (1991) Inlet of alkaline river water into peaty lowlands: effects on water quality and *Stratiotes aloides* L. stands. Aquat. Bot. **39:** 267–293


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