

1 **Biogenic production of DMSP and its degradation to DMS – their**
2 **roles in the global sulfur cycle**

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16 Running title: DMSP biosynthesis and catabolism

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18 **ABSTRACT**

19 Dimethyl sulfide (DMS) is the most abundant form of volatile sulfur in Earth's
20 oceans, and is mainly produced by the enzymatic cleavage of
21 dimethylsulfoniopropionate (DMSP). DMS and DMSP play important roles in driving
22 the global sulfur cycle and may affect climate. DMSP is proposed to serve as an
23 osmolyte, a grazing deterrent, a signaling molecule, an antioxidant, a cryoprotectant
24 and/or as a sink for excess sulfur. It was long believed that only marine eukaryotes such
25 as phytoplankton produce DMSP. However, we recently discovered that marine
26 heterotrophic bacteria can also produce DMSP, making them a potentially important
27 source of DMSP. At present, one prokaryotic and two eukaryotic DMSP synthesis
28 enzymes have been identified. Marine heterotrophic bacteria are likely the major
29 degraders of DMSP, using two known pathways: demethylation and cleavage. Many
30 phytoplankton and some fungi can also cleave DMSP. So far seven different prokaryotic
31 and one eukaryotic DMSP lyases have been identified. This review describes the global
32 distribution pattern of DMSP and DMS, the known genes for biosynthesis and cleavage
33 of DMSP, and the physiological and ecological functions of these important
34 organosulfur molecules, which will improve understanding of the mechanisms of
35 DMSP and DMS production and their roles in the environment.

36 **Key words:** marine microorganism; dimethylsulfoniopropionate (DMSP); dimethyl
37 sulfide (DMS); DMSP biosynthesis; DMSP cleavage

38

39 INTRODUCTION

40 The biogenic trace gas dimethyl sulfide (DMS) is the dominant natural source of
41 volatile organic sulfur compounds emitted into the atmosphere from the marine
42 environment (Charlson et al., 1987; Andreae, 1990; Simó, 2001; Stefels et al., 2007).
43 The amount of sulfur (in the form of DMS) transferred from ocean to atmosphere is
44 approximately 13–37 Tg annually (Ksionzek et al., 2016).

45 DMS emissions not only balance the global sulfur budget, but may also impact
46 Earth's climate through its oxidation products in the atmosphere (Figure 1). When DMS
47 diffuses into the atmosphere, it can be rapidly oxidised by OH (during the day) and NO₃
48 (at night) radicals to form various sulfur-containing products, such as sulfur dioxide
49 (SO₂), methanesulfonic acid (MSA) and non-sea-salt sulfate (nss-SO₄²⁻) (Andreae et
50 al., 1985; Boucher and Pham, 2002). Sulfate produced by this process not only increases
51 the natural acidity of atmospheric deposition, but also contributes to cloud condensation
52 nuclei (CCN) in remote marine environments (Quinn and Bates 2011; Charlson et al.
53 1987). Changes in CCN concentration affect the cloud droplet number and
54 concentration, which influences cloud albedo and potentially affects global temperature
55 (Charlson et al., 1987). However, the contradictory view has also been proposed that a
56 DMS biological control over CCN probably does not exist and the bioregulation of
57 DMS on climate has been exaggerated (Quinn and Bates, 2011).

58 The main precursor of DMS is dimethylsulfoniopropionate (DMSP), an organic
59 sulfur compound that is produced in prodigious amounts (2.0 petagrams sulfur annually,
60 worldwide) by many marine organisms, thought mainly to be including marine
61 phytoplankton (Figure 1; Keller et al., 1989; Stefels et al., 2007; Ksionzek et al. 2016).
62 Upon the release of intracellular DMSP into the environment, it can be taken up by a
63 wide range of microorganisms (Malmstrom et al., 2004; Vila et al., 2004; Raina et al.,
64 2017) and catabolised as a source of carbon, reduced sulfur and/or energy (Reisch et
65 al., 2013; Raina et al., 2009; Tripp et al., 2008). DMSP is cleaved to produce DMS and
66 the co-products acrylate or 3-hydroxypropionate (3-HP) by intracellular algal or
67 bacterial DMSP-lyase enzymes (Figure 1; Curson et al., 2011; Johnston et al., 2016). It
68 is thought that only a minor fraction of dissolved DMSP, varying between 2% and 21%,
69 is enzymatically cleaved to liberate DMS (Kiene and Linn, 2000). The majority of
70 DMSP is likely demethylated by bacterial activity, and does not lead to the formation
71 of DMS, but instead can lead to the generation of the trace gas methanethiol (MeSH;
72 Kiene and Linn, 2000; Yoch, 2002; Howard et al., 2006).

73 In all known DMSP synthesis pathways, DMSP is synthesised from the amino acid
74 L-methionine (Met), and is likely more abundant in marine than terrestrial
75 environments because of the high concentration of sulfate in seawater (Stefels, 2000).

76 The marine organisms that make DMSP include single-celled phytoplankton (such as
77 dinoflagellates, diatoms and coccolithophores) (Keller et al., 1989; Curson et al., 2018;
78 Kageyama et al., 2018), some red and green algae (Challenger and Simpson, 1948;
79 Greene, 1962), a few angiosperms (Otte et al., 2004), as well as some corals (Raina et
80 al., 2013). More recently, it has been found that marine heterotrophic bacteria can also
81 make DMSP, making them a potentially important source of marine DMSP (Curson et
82 al., 2017).

83 DMSP is proposed to serve numerous physiological functions in organisms that
84 accumulate it under different environmental conditions (Otte et al., 2004). Its specific
85 function may vary in different organisms, perhaps based on where DMSP is localised
86 in the cell (Trossat et al., 1996, 1998). For example, DMSP detected in the chloroplasts
87 of the angiosperm *Wollastonia* was considered to contribute significantly to chloroplast
88 osmoregulation and may protect photosynthetic processes from stress (Trossat et al.,
89 1998). Furthermore, DMSP also acts as a carbon, sulfur and/or energy store and its
90 synthesis may prevent the depletion of important nitrogen precursors during periods of
91 nitrogen limitation (Stefels et al., 2000).

92 In this Review, we focus on the distribution pattern of DMSP and DMS in the
93 marine environment, the relative contributions of marine phytoplankton and bacteria to
94 the production of DMSP and its degradation to DMS, the physiological function of
95 DMSP and DMS and their roles in the global sulfur cycle.

96 **DISTRIBUTION OF DMSP AND DMS IN THE MARINE ENVIRONMENT**

97 DMSP is ubiquitous in the euphotic layers of the marine system, with a wide
98 variation in concentrations ranging from low nanomolar to several micromolar
99 concentrations (Table 1). DMS is produced mainly from the cleavage of DMSP, but can
100 also be produced from DMSP-independent sources (Carrión et al., 2015, 2017). To a
101 certain extent, the distributions of DMSP and DMS show similar variation patterns in
102 the surface ocean. Here we summarise many of the surveys of global DMSP and DMS
103 distribution in last 30 years from 1988 to 2018 (Table 1). The concentration of total
104 DMSP (DMSP_t) was always less than 1.78 μM in seawater. The majority of DMSP is
105 found within microorganisms, termed ‘particulate DMSP’ (DMSP_p; $\leq 1.74 \mu\text{M}$), whilst
106 the available DMSP, ‘dissolved DMSP’ (DMSP_d), concentrations are lower at ≤ 275
107 nM.

108 **Spatial characteristics**

109 On a global scale, in polar and subpolar regions, higher DMS and DMSP
110 concentrations are always observed (Table 1). In Arctic Ocean (e.g., Northeast Atlantic
111 and Norwegian and Greenland Seas) surface seawater, DMS concentrations were
112 observed up to 93.8 nM, while DMSP_p and DMSP_d were up to 282.4 nM and 199 nM,

113 respectively, likely due to the phytoplankton blooms arising during seasonal sea ice
114 melting (Malin et al., 1993; Li et al., 2015). Relatively high DMS and DMSP
115 concentrations also occurred in the Ross Sea (Rellinger et al., 2009), the West Antarctic
116 Peninsula (Stefels et al., 2018) and Canadian subarctic and arctic marine water
117 (Jarníková et al., 2018) as shown in Table 1.

118 In high-latitude and temperate regions, high DMS and DMSP concentrations, so-
119 called “hotspots”, coincide with the high primary productivity ocean areas. In the East
120 China continental sea, the average DMS, DMSPd and DMSPp concentrations in
121 summer are observed at 5.3 nM, 5.2 nM and 27.1 nM, respectively (Zhang et al., 2014).
122 High concentrations of DMSP are also reported in the Gulf of Maine (Matrai et al.,
123 1993) and Gulf of Saint Lawrence (Cantin et al., 1996). In addition, a study of the
124 Belgian coastal zone showed relatively high phytoplankton biomass levels occurred in
125 the coastal upwelling areas because of the vertical supply of nutrients, and this was
126 accompanied by high DMS and DMSP concentrations, with concentrations of DMSPt
127 up to 1.78 μ M and DMS up to 270 nM (Speeckaert et al., 2018). High concentrations
128 of DMS and DMSPp are also reported in waters off the western coast of Ireland, up to
129 42 nM and 50 - 635 nM respectively (Locarnini et al., 1998). The tropical oceans show
130 moderate and relatively constant DMS concentrations throughout the year (Bates and
131 Quinn, 1997).

132 The vertical distribution of DMS and DMSP in seawater generally exhibit
133 decreasing trends from the surface waters to the deeper waters (Table 1). Maximum
134 DMS and DMSP concentrations are usually found in surface seawater or in seawater <
135 100 m below the surface, but are reduced in the marine euphotic zone. Since
136 phytoplankton are widely recognised as the major producers of DMSP in the marine
137 environment, it is not surprising that vertical distribution patterns of DMSP and DMS
138 resemble those of phytoplankton.

139 **Seasonal cycle pattern**

140 In both hemispheres, DMSP and DMS concentrations exhibit similar seasonal
141 cycle patterns in relation to changes in temperature and light. That is, the DMS and
142 DMSP concentrations rise in spring and usually peak in late summer, and then decrease
143 through autumn and winter. These temporal distribution variations are particularly
144 apparent in middle-high latitude ocean regions, such as the North Pacific Ocean where
145 the average DMS concentration reaches the maximum (> 5 nM) in the summer and
146 drops to the minimum (< 1 nM) in the winter (Aranami and Tsunogai, 2004). In the
147 Yellow-East China Sea, the concentration of DMSP was lowest (6.5-18.0 nM) during
148 winter, and highest in summer (7.6-234.9 nM), and slightly higher in autumn (7.4-91.0
149 nM) than in spring (5.5-73.7 nM) (Yang et al., 2006, 2011, 2012; Zhang et al., 2014,
150 2017). Moving towards the equator, this seasonal cycle pattern gets less pronounced

151 and even disappears, consistent with the associated reduction in seasonality meaning
152 decreasing variation in temperature or day length. In the tropical oceans around the
153 equator, the average concentrations of DMS and DMSP are reasonably constant
154 throughout the year.

155 Diurnal cycles of DMS and DMSP concentrations are also present. Song et al.
156 (2014) reported DMSP concentrations in off-shore areas were higher in the daytime
157 than at night, and the DMS concentration peaked in the afternoon and reached the
158 minimum in the early morning.

159 **Effect of environmental factors on DMSP and DMS distribution**

160 The distribution of DMSP and DMS in seawater is affected by various physical,
161 chemical and biological factors. In the Norwegian Sea and the Greenland Sea,
162 chlorophyll *a* concentration (indicator of phytoplankton biomass) was shown to be the
163 most significant impact factor in DMSP production, followed by seawater temperature
164 and salinity (Li et al., 2015). In marginal seas, anthropogenic factors, such as
165 atmospheric pollution, may play important roles in the production of DMSP and DMS
166 (Yang et al., 2015). In addition, nitrogen availability is well known as a major
167 influencing factor in increasing intracellular levels of DMSP in marine phytoplankton
168 (Keller et al., 1996; Sunda et al., 2007; Curson et al 2018). Nutrients like silicate could
169 indirectly affect DMSP production through a significant effect on the growth of larger
170 nanoplankton (Zhai et al., 2018). Solar radiation is also well known as an important
171 driver of DMS dynamics in the ocean (Vallina and Simó, 2007). Biologically, as the
172 driving force on DMSP degradation, the biomass and composition of bacteria in the
173 marine environment have vital influence on DMS production. It is possible that all these
174 factors, such as nutrient levels and solar radiation, may affect phytoplankton biomass,
175 which are the direct factors affecting DMSP and DMS concentrations.

176 The DMS and DMSP temporal cycle pattern is usually associated with the biomass
177 of phytoplankton, particularly the high DMSP-producing taxa, e.g., dinoflagellates and
178 prymnesiophytes (Keller, 1989). Higher phytoplankton biomass and biological
179 activities are found during the warmer and more illuminated seasons, which leads to
180 more DMSP and more of its bio-degradation product, DMS. Townsend and Keller
181 (1996) found that concentrations of DMSPp were related more to the presence of
182 specific phytoplankton species rather than to overall phytoplankton biomass. The study
183 of Scarratt et al (2002) in the northwest Atlantic also showed statistically significant
184 correlations between the abundance of dinoflagellates and prymnesiophytes and the
185 concentrations of DMS(P). In the region with the highest DMS(P) concentrations, the
186 phytoplankton assemblage was dominated by *Chrysochromulina* spp. (prymnesiophyte)
187 and *Gyrodinium flagellare* (dinoflagellate) whose abundance showed a marked
188 correlation with total DMSPp as well as the 2 to 11 μm size fraction of DMSP. In

189 addition, Archer et al. (2009) discovered a taxonomic succession of high DMSP-
190 producing phytoplankton is apparent in the seasonal pattern of DMSPt concentrations.
191 Peridinin and DMSPt concentrations showed similar seasonal trends, which illustrates
192 the substantial contribution by the dinoflagellate taxa to DMSP production. However,
193 in low-latitude temperate and northern subtropical areas, DMS exhibits high levels in
194 the summer, when phytoplankton biomass is low, and this has been coined the “DMS
195 summer paradox” (Simó and Pedrós-Alió, 1999). The possible reason(s) might be both
196 or either: 1) taxonomic succession from minor to major DMSP-producing
197 phytoplankton as previously proposed (Simó and Pedrós-Alió, 1999); 2) blooming of
198 DMSP-producing bacterial taxa which were found in our recently discovery (Curson et
199 al., 2017).

200 **BIOSYNTHESIS OF DMSP**

201 Biosynthesis of DMSP has been identified in some plants, macroalgae,
202 phytoplankton, corals (Reed, 1983; Keller et al., 1989; Paquet et al., 1994; Hanson et
203 al., 1994; Kocsis et al., 1998; Otte et al., 2004; Raina et al., 2013; Ausma et al., 2017),
204 and most recently also discovered in many marine bacteria (Table 2; Curson et al., 2017).
205 Thus, DMSP is present in all marine ecosystems and can be utilised not only by the
206 producing organisms, but also by other species that live in the same habitats with the
207 producers.

208 **Biosynthesis of DMSP by marine eukaryotes**

209 DMSP was first identified in 1948 in the red alga *Polysiphonia* (Challenger &
210 Simpson, 1948). The main DMSP producers are widely recognised to be marine
211 phytoplankton, and strains in the classes of Dinophyceae (dinoflagellates) and
212 Prymnesiophyceae (haptophytes) were recorded with high intracellular DMSP
213 concentrations of up to 10^2 - 10^3 mM (Keller, 1989; Stefels, 2000). As well as these very
214 high producers, DMSP biosynthesis has also been documented in other marine algae,
215 e.g. diatoms (Lyon et al., 2011; Kettles et al., 2014), the green alga *Ulva intestinalis*
216 (Gage et al., 1997), and some higher plants like sugarcane (Paquet et al., 1994) and the
217 coastal angiosperms *Spartina alterniflora* (Kocsis et al., 1998) and *Wollastonia biflora*
218 (Hanson et al., 1994). The green tide (*Ulva* bloom), which occurs annually in the
219 summer in the Yellow Sea and East China Sea (Figure 2), always brings with it a tangy
220 odour (DMS is one of the compounds contributing to the complex smell) during the
221 algal decay process. Recently, DMSP biosynthesis was also reported in the kingdom of
222 animalia with two corals species *Acropora millepora* and *Acropora tenuis* shown to
223 produce DMSP (Raina et al., 2013). The occurrence of DMSP in corals was previously
224 attributed to the DMSP-producing coral symbiont *Symbiodinium*, but investigations of
225 algal-free juvenile corals clearly demonstrated a heat stress-dependent DMSP
226 production by the marine invertebrates themselves (Raina et al., 2013). Orthologues of

227 the eukaryotic *DSYB* DMSP biosynthesis gene present in the genome of the coral
228 *Acropora cervicornis* were shown to encode a functional SAM-dependent
229 methyltransferase, catalyzing the key enzymatic step in DMSP biosynthesis via the
230 transamination pathway (Curson et al., 2018).

231 At present, it is known that DMSP synthesis in marine eukaryotes can occur
232 through four different pathways, two methylation pathways in angiosperms (Hanson
233 and Gage, 1996; Kocsis et al., 1998), a transamination pathway in diatoms,
234 dinoflagellates, haptophytes, green algae and corals (Gage et al., 1997; Summers et al.,
235 1998; Raina et al., 2013; Curson et al., 2018) and a decarboxylation pathway in one
236 dinoflagellate (Uchida et al., 1996). Each of the proposed pathways for DMSP
237 biosynthesis begins with methionine, although subsequent steps vary (Figure 3). Since
238 the biosynthesis reactions and enzymes evolved are quite diverse, these different DMSP
239 biosynthetic pathways must have evolved independently. However, it is unknown
240 whether some taxonomically distinct organisms such as green algae, diatoms,
241 dinoflagellates, haptophytes and corals use the same transamination pathway due to a
242 horizontal gene transfer event or due to their evolving independently. DMSP production
243 has been found to be species-specific, with some members of a genus producing it and
244 others not, and can vary by three orders of magnitude within phytoplankton groups. The
245 highest intracellular concentrations are typically reported in dinoflagellates and
246 haptophytes and lower concentrations in diatoms (Table 2; Keller, 1989).

247 Although it has long been known that eukaryotic algae can produce DMSP, the lack
248 of genomic sequences and molecular tools for studying marine eukaryotes meant that
249 the functional genes have only recently been identified. Todd and colleagues, based on
250 work in bacteria (see below), identified the *DSYB* gene, encoding a SAM-dependent
251 methyltransferase, in many marine algae, including dinoflagellates, diatoms and
252 coccolithophores, as well as in some corals. *DSYB* mediates the key step of the
253 transamination pathway, transforming 4-methylthio-2-hydroxybutyrate (MTHB) to 4-
254 dimethylsulfonio-2-hydroxybutyrate (DMSHB; Table 2; Curson 2018). Takabe and
255 colleagues have recently found the isozyme of *DSYB* in the diatom *Thalassiosira*
256 *pseudonana*, named TpMMT (Table 2), encoded by the *TpMT2* gene, which showed no
257 significant homology with ratified *DSYBs* (Kageyama et al., 2018). DMSP synthesis
258 genes involved in steps other than S-methylation have not been identified in any
259 organisms so far.

260 **Biosynthesis of DMSP by marine bacteria**

261 Recently, DMSP biosynthesis was detected in *Labrenzia aggregata* LZB033
262 (Figure 4) and then also in several other marine *Alphaproteobacteria*, including
263 *Oceanicola batsensis* HTCC2597, *Pelagibaca bermudensis* HTCC2601,
264 *Sediminimonas qiaohouensis* DSM21189, *Amorphus coralli* DSM18348, *Sagittula*

265 *stellata* E-37, *L. aggregata* IAM12614, and *Thalassobaculum salexigens* DSM19539
266 (Table 2; Curson et al., 2017). These bacteria synthesise DMSP through the
267 transamination pathway, the same pathway used by many marine algae and some corals.
268 Through screening an *L. aggregata* LZB033 genomic library for candidate DMSP
269 biosynthesis genes, one gene *dsyB*, encoding a functional MTHB methyltransferase,
270 was identified as the key gene in bacterial DMSP biosynthesis. The transfer of the *dsyB*
271 gene alone was sufficient to confer the ability to synthesise DMSP to the non-DMSP
272 producing bacterium *Rhizobium leguminosarum*. This indicates that enzymes
273 catalyzing the production of MTHB and the decarboxylation of DMSHB (see Fig 3)
274 are not specific to DMSP production. The DsyB protein is a SAM-dependent
275 methyltransferase and is encoded by the genomes of ~100 marine *Alphaproteobacteria*
276 (E-value $\leq 5 \times 10^{-69}$). DsyB has relatively low similarity to the eukaryotic DSYB (E-
277 values $\leq 1 \times 10^{-30}$), but this low level of similarity was still sufficient to allow the
278 subsequent identification of the eukaryotic *DSYB* gene described above. Environmental
279 conditions known to affect DMSP production in marine phytoplankton, like increased
280 salinity, nitrogen availability, and low temperatures, were also shown to upregulate the
281 expression of the bacterial *dsyB* gene, as well as the production of DMSP in *L.*
282 *aggregata* LZB033 (Curson et al., 2017). The acquisition of *dsyB* by some bacteria, and
283 consequently the ability to synthesise DMSP, may confer a competitive advantage in
284 the marine environment, where bacteria must contend with, for example, salinity and
285 low nitrogen availability.

286 Phylogenetic analysis of eukaryotic DSYBs and alphaproteobacterial DsyBs
287 showed that DSYB and DsyB sequences formed two distinct sister branches, but not
288 all major algal groups have *DSYB* in their genomes (Curson et al., 2018). According to
289 these facts, the authors concluded that eukaryotic DSYBs originated from bacterial
290 DsyBs early in their evolution and they were obtained either: 1) through endosymbiosis
291 of the mitochondrial ancestor, which led to alphaproteobacterial genes making up a
292 significant proportion in eukaryotic genomes (Ku et al., 2015), and then DSYB has
293 been lost by some of the eukaryotes; or 2) more recently by multiple horizontal gene
294 transfer (HGT) events (Curson et al., 2018).

295 **DMSP CLEAVAGE AND DMS PRODUCTION**

296 After biosynthesis, some of the produced DMSP can be cleaved to DMS and
297 acrylate (or 3-HP) by the DMSP-producer themselves (Alcolombri et al., 2015; Curson
298 et al., 2017). However, the vast majority of the DMSP is catabolised after it is released
299 into the water column in the form of dissolved DMSP (DMSPd), and utilised by other
300 heterotrophic microorganisms, predominantly bacteria (Zubkov et al., 2001). The
301 corresponding enzymes that catalyse DMSP cleavage are called DMSP lyases. They
302 exist in both eukaryotes and bacteria. There is high biodiversity in the bacterial DMSP
303 lyases, which belong to three distinct protein superfamilies, while the only known

304 eukaryotic DMSP lyase Alma1 bears no resemblance to any of the bacterial ‘Ddd’
305 DMSP lyases (Table 3).

306 **Cleavage of DMSP by heterotrophic bacteria**

307 Although many marine phytoplankton degrade some of the DMSP that they
308 produce (Stefels 2000), most of the microbial DMSP catabolism is thought to occur
309 following its release into the dissolved organic matter pool caused by viral lysis,
310 zooplankton grazing or senescence of the algal cells. Here, it is available for
311 assimilation and degradation by free-living bacterioplankton or attached bacteria
312 (Kiene et al., 2000).

313 Marine bacteria catabolise DMSP via two competing pathways, the demethylation
314 pathway (accounting for the majority of DMSP degradation; Kiene et al 2000) and the
315 cleavage pathway. The demethylation pathway can yield the reactive gas methanethiol
316 (MeSH). The key enzyme DmdA, which belongs to the glycine cleavage T-protein
317 (GcvT) superfamily, catalyses the first step in the DMSP demethylation pathway
318 (Howard et al., 2006; Reisch et al., 2008), and genes for the subsequent steps of the
319 DMSP demethylation pathway have also been fully elucidated by the Moran laboratory
320 (Reisch et al., 2011a, 2011b, 2013; Moran et al., 2012). DMSP demethylation is a major
321 biological control on DMS formation because it directly competes with the cleavage
322 pathway. The cleavage pathway produces the climatically relevant volatile DMS via
323 DMSP lysis or hydrolysis (González et al., 1999), which will be described in detail here.

324 Currently, seven bacterial DMSP cleavage genes *dddD*, *-L*, *-P*, *-Q*, *-W*, *-Y* and *-K*
325 have been identified, and the enzymes they encode mediate the cleavage of DMSP to
326 DMS (Curson et al., 2011a; Johnston et al., 2016; Sun et al., 2016). These genes are
327 found in various bacterial taxa. *dddD* is present in some *Gammaproteobacteria*,
328 especially in *Oceanospirillales* and *Pseudomonadales*, and also in some other
329 *Proteobacteria*, like *Rhizobiales* and *Rhodobacterales* (both *Alphaproteobacteria*) and
330 *Burkholderiales* (*Betaproteobacteria*). *dddL*, *-P*, *-Q*, and *-W* are mainly found in the
331 *Rhodobacteraceae* family of *Alphaproteobacteria*, with *dddP* also present in some
332 eukaryotic fungi (Todd et al., 2009; Kirkwood et al., 2010). *dddY* was identified in the
333 betaproteobacterium *Alcaligenes faecalis* strain M3A and is found in other
334 *Proteobacteria*, i.e. *Gammaproteobacteria*, *Deltaproteobacteria* and
335 *Epsilonproteobacteria* (Curson et al., 2011b; Li et al., 2017). *dddK* was identified in
336 *Pelagibacter ubique* HTCC1062, which belongs to the most abundant marine bacterial
337 group — the SAR11 clade (Sun et al., 2016). Among these bacterial *ddd* genes, *dddP*
338 and *dddQ* are the two most abundant ones in marine metagenomes (Curson et al., 2018).

339 Interestingly, the protein products of these *ddd* genes differ both in size and amino
340 acid sequence and belong to distinct polypeptide families. DddL/Q/W/K/Y belong to
341 the cupin superfamily (Table 3; Lei et al., 2018), and all catalyse DMSP lysis into DMS

342 and acrylate. Biochemical and crystal structural studies revealed that DddQ, DddW,
343 DddK and DddY all need metal cofactors, but that there is variability between which
344 metal works best for each enzyme. For example, based on its crystal structure, DddQ
345 from *Ruegeria lacuscaerulensis* ITI_1157 is bound to Zn (II), whereas the addition of
346 exogenous Co (II) and Mn (II) can effectively enhance its activity (Li et al., 2014),
347 while Brummet et al. (2016) proposed that the addition of Zn (II) can inhibit its activity
348 and that Fe (III) is the appropriate co-factor. DddQ is clearly promiscuous in which
349 metal co-factor it requires for activity. Based on biochemical studies, DddW from *R.*
350 *pomeroyi* DSS-3 showed the highest enzyme activities with Fe (II) or Mn (II) as
351 cofactors (Brummet et al., 2015); DddK from *Pelagibacter* can be activated by the
352 presence of Fe (II) and Ni (II) (Schnicker et al., 2017). DddY from the
353 gammaproteobacterium *Acinetobacter bereziniae* contains a catalytic domain with Zn
354 (II) as cofactor (Li et al., 2017). Protein sequences of DddL show conserved active site
355 residues with the other cupin DMSP lyases for metal cofactor binding, but enzymatic
356 or structural biological studies on DddL have not been reported. DddP belongs to the
357 M24B metallopeptidase family (Todd et al., 2009), and, like the cupin lyases, catalyses
358 the cleavage of DMSP to DMS and acrylate. A study on the catalytic mechanism of
359 DddP from *R. lacuscaerulensis* ITI_1157 revealed that mature DddP protein is a stable
360 dimer and undergoes an Fe ion shift during the process of DMSP cleavage (Wang et al.,
361 2015). DddD belongs to the class III CoA-transferase family (Todd et al., 2007), and is
362 the only characterised Ddd that cleaves DMSP by hydrolysis and produces DMS and
363 3-HP or 3-HP-CoA (Todd et al., 2007; Alcolombri et al., 2014). Although, all the above
364 Ddd enzymes can act on DMSP, liberating DMS, only DddD, DddY and DddL have
365 high specific DMSP lyase activities (K_{cat}/K_m ; 318 $M^{-1} s^{-1}$ for DddD; $10^{5-6} M^{-1} s^{-1}$ for
366 DddY and $1.66 \times 10^6 M^{-1} s^{-1}$ for DddL), whilst the other Ddd lyases have much lower
367 specific DMSP lyase activities (Alcolombri et al., 2014; Brummett et al., 2015; Lei et
368 al., 2018). It should be noted though that much of the enzyme work is carried out with
369 proteins overexpressed and purified from *Escherichia coli* and not from the natural host.
370 What effects this has on the activity of the enzymes and their metal content is not always
371 determined. The three-carbon moiety of DMSP, transformed to acrylate or 3-HP during
372 the cleavage process, can then enter in central carbon catabolism (Todd et al., 2010,
373 2012b; Curson et al., 2011, 2014; Reisch et al., 2011b, 2013; Asao and Alber, 2013).

374 Within the *Tara* Oceans metatranscriptome data sets apportioned to marine
375 bacteria, *dddP*, *dddK*, *dddQ*, *dddD* and *dddL* transcripts were always detected, and were
376 far more abundant than *dddY* and *dddW*, which was not detected (Curson et al., 2018).
377 These results indicate that most of these bacterial DMSP cleavage genes are expressed
378 in nature.

379 **Cleavage of DMSP by phytoplankton**

380 It has been known for many years that marine phytoplankton can cleave DMSP

381 into DMS and acrylate (Table 3; Yoch, 2002), but a eukaryotic DMSP lyase gene,
382 Alma1, was only identified recently by Alcolombri et al. (2015), in the haptophyte
383 *Emiliania huxleyi*. Its product Alma1, which belongs to the aspartate racemase
384 superfamily, generates DMS and acrylate from DMSP like the majority of the bacterial
385 Ddd lyases (Table 3; Alcolombri et al., 2015). Based on protein sequence similarity,
386 orthologues of Alma1 (and its paralogues) are present in a wide range of eukaryotes,
387 including haptophytes, dinoflagellates and corals, highlighting a wide taxonomic
388 distribution for this protein (Alcolombri et al., 2015). Alma1-like proteins of lesser
389 sequence similarity are also present in some bacteria. Only Alma1 enzymes from *E.*
390 *huxleyi* and *Symbiodinium* have been shown to have high DMSP lyase activity. Other
391 homologues with lesser protein sequence similarity to the Alma1 from *E. huxleyi*, from
392 the haptophyte *Phaeocystis antarctica* and the coral *A. millepora*, have extremely low
393 DMSP lyase activities (<0.03 % of the activity of the *Symbiodinium* Alma1 homologue
394 and not much above the negative control) (Alcolombri et al., 2015). Thus, functional
395 predictions based solely on sequence similarity are still very difficult and this makes
396 predictions of their environmental importance very difficult without more functional
397 ratification. Many other eukaryotes, like species in Chlorophyta, Rhodophyta and
398 Alveolata, are also known to cleave DMSP into DMS and acrylate (Cantoni and
399 Anderson, 1956; Stefels et al. 1993, 1995; Nishiguchi and Goff, 1995; Steinke et al.,
400 2002; Yoch, 2002; Yost and Mitchelmore, 2009; Franklin et al., 2010; Niki et al., 2000),
401 but the genes involved have not yet been identified, and further effort will be needed to
402 uncover these.

403 **FUNCTIONS OF DMSP AND DMS**

404 **Ecological roles**

405 Marine microorganisms encounter and import DMSP in their natural habitat. They
406 incorporate its sulfur into amino acids and utilise its three-carbon moiety for energy,
407 which underlines the role of DMSP as one of the most important sulfur and carbon
408 sources for many marine bacteria. Some bacteria, like SAR11, seem to be adapted to
409 the use of reduced sulfur compounds such as DMSP, which represents the main
410 ecologically relevant sulfur source that these bacteria are able to utilise, and genes for
411 prominent alternative pathways for sulfur metabolism, such as sulfate reduction, have
412 been lost (Tripp et al., 2008).

413 The process in which DMSP is degraded to DMS is also of great global
414 significance as mentioned above. DMS is volatile and has low solubility, and is thus
415 emitted in large amounts ($\sim 3 \times 10^7$ tonnes per annum) from the oceans into the
416 atmosphere. This represents the largest natural source of atmospheric sulfur and the
417 major route for the transfer of sulfur from the oceans to the air, and contributes
418 substantially to the global sulfur flux. DMS oxidation products, e.g., SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$,

419 $\text{S}_4\text{O}_6^{2-}$ and DMSO, display longer residence time in the atmosphere than
420 anthropogenically-derived SO_2 , and thus their contribution to the global sulfur burden
421 is also greater (Lovelock et al., 1972; Chin and Jacob, 1996).

422 In the air, these DMS oxidation products act as condensation nuclei, causing water
423 molecules to coalesce and form clouds. When returned to land via precipitation, this
424 helps to bring marine sulfur to the continents, completing the global sulfur cycle since
425 SO_4^{2-} is transported from land via rivers to the oceans. The return of sulfur from the
426 ocean to the land requires atmospheric sulfur volatiles, and DMS is the paramount
427 compound among them. DMS-derived SO_4^{2-} in the atmosphere acts in CCN formation,
428 as described above, and the resulting increased cloud cover may influence local and
429 possibly even global albedo, with a cooling effect on the climate (Figure 1 and Table 4;
430 Kettle and Andreae, 2000; Simó, 2001). A negative feedback model has been suggested,
431 in which the cooling effect due to increased DMS emission leads to a slower biomass
432 production and thus a decreased production of DMSP and then its catabolite, DMS.
433 This would then cause a consequent decrease in the cooling effect and increase in
434 biomass production to complete the feedback loop (Charlson et al., 1987). However,
435 this model has been challenged recently (Quinn and Bates, 2011).

436 **Physiological and biological functions**

437 Besides the great importance of DMSP and DMS in biogeochemical cycles and
438 their potential effects on climate, these organosulfur molecules also have miscellaneous
439 suggested physiological and biological functions in various marine species (Table 4).
440 However there is little evidence at a molecular genetic level to verify these putative
441 functions in any organism despite many of the proposed roles for these compounds
442 being strongly suggested to be beneficial to phytoplankton and bacteria for survival in
443 the marine environment.

444 **DMSP**

445 In phytoplankton and green algae, DMSP is proposed to have roles as an
446 osmoprotectant, a cryoprotectant, a grazing deterrent, an antioxidant, a sink for excess
447 sulfur, as well as other biological functions (Table 4).

448 For the organisms with high intracellular DMSP concentrations, this metabolite is
449 present at physiologically relevant levels sufficient to be considered a major osmolyte,
450 helping cells to overcome the adverse environment of hyperosmosis. For example,
451 when exposed in high salt conditions, the intracellular DMSP concentration in
452 *Hymenomonas carterae* cells can be as high as 300 mM (Vairavamurthy et al., 1985;
453 Kirst, 1990). In many DMSP-producers, DMSP is likely not the major osmolyte, with
454 e.g. some nitrogen-containing osmolytes like glycine betaine, choline and carnitine
455 adopting this function (Dickschat et al., 2015). DMSP was investigated for its

456 cryoprotective activity on the model enzymes lactate dehydrogenase (LDH) and malate
457 dehydrogenase (MDH), which were extracted from the polar alga *Aerosiphonia arela*
458 (Chlorophyta; Karsten et al., 1996). Both of the activities and stabilities of LDH and
459 MDH under freezing conditions were risen with the addition of DMSP. DMSP produced
460 by *E. huxleyi*, and its degradation products acrylate and acryloyl-CoA, have certain
461 toxic effects on many organisms, and are thought to act as predator deterrents, thus
462 increasing the chance of *E. huxleyi* survival (Wolfe and Steinke, 1996; Wolfe et al.,
463 1997). DMSP and its breakdown products, e.g., DMS, acrylate, DMSO and acrylate
464 can scavenge hydroxyl radicals and other reactive oxygen species, and thus they may
465 serve as highly effective antioxidants (Sunda et al., 2002; Lesser 2006; Husband et al.,
466 2012; Curson et al., 2018). DMSP biosynthesis is suggested to provide sinks for the
467 excess energy, carbon and reducing equivalents derived from active photosynthesis,
468 saving nitrogen for cell growth and accelerating sulfate uptake from the environment
469 (Gage et al., 1997; Stefels, 2000; Bullock et al., 2017).

470 DMSP can also be a signal molecule, attracting specific groups of bacteria and
471 structuring the microbial communities that are integrally associated with corals and
472 other organisms, underpinning their health (Raina et al., 2013). Similarly, it can attract
473 several phytoplankton and bacterivore and herbivore microzooplankton (Seymour et al.,
474 2010). Apart from these microorganisms, DMSP can provide underwater foraging cues
475 for some reef fish (DeBose et al., 2008). As a chemical signaling molecule, DMSP may
476 induce bacterial quorum sensing, e.g., participating in the degradation of particulate
477 organic matter (POC) (Seyedsayamdost et al., 2011; Johnson et al., 2016). As a
478 mediator of bacterial virulence, DMSP may regulate the demise of *E. huxleyi* blooms
479 (Barak-Gavish et al., 2018).

480 **DMS**

481 DMS is the cue for chemosensory attraction for marine invertebrates and bacteria
482 that feed on DMSP-producing phytoplankton (Table 4; Zimmer-Faust et al., 1996;
483 Steinke et al., 2006). In addition, as mentioned above, the grazing zooplankton cause
484 the degradation of algal DMSP to DMS and acrylate, which act as feeding deterrents
485 towards the protozoan herbivores, thus representing a chemical defense mechanism of
486 the phytoplankton (Wolfe and Steinke, 1996; Wolfe et al., 1997). The resulting
487 increased emission of DMS into the atmosphere upon grazing is in turn also recognised
488 by seabirds that feed on the grazing zooplankton (Nevitt and Bonadonna, 2005).

489 **CONCLUSION AND PROSPECT**

490 In summary, DMS and DMSP play important roles in driving global sulfur cycling
491 and may affect climate. It is now clear that both prokaryotes (e.g., bacteria) and
492 eukaryotes (e.g., algae) can synthesise and degrade DMSP. However, their relative
493 contributions to environmental DMSP production and cleavage have not been clearly

494 quantified, and the ways in which they are affected by and impinge on environmental
495 parameters has not been elucidated either. Since it has long been thought that DMSP
496 can only be produced by marine photosynthetic organisms, studies on the distribution
497 and concentration of DMSP and DMS were mainly limited to the marine euphotic
498 layers, while in the deeper ocean and sediments, they have been largely ignored.
499 According to the limited data available (Curran et al., 1998; Li et al., 2015; Zhai et al.,
500 2018), absolute concentrations of DMSP and DMS in the deeper ocean are relatively
501 low, but on a global scale, DMSP and DMS in deep oceans should be investigated
502 further due to the immense water volume and bacterial biomass in this biosphere.

503 Considering heterotrophic bacteria are chemoheterotrophic and that
504 phytoplankton are photoautotrophic, we propose the hypothesis that phytoplankton are
505 only the major contributor to DMSP production at euphotic depths, while in deeper
506 oceans where limited or even no sunlight penetrate, the relative contribution of
507 heterotrophic bacteria to DMSP production may become dominant.

508 Since the discovery of DMSP biosynthesis in marine heterotrophic bacteria and
509 the identification of the key gene *dsyB* in this process, many other heterotrophic bacteria
510 have also been found to produce DMSP. However, among some of the genomes of these
511 newly discovered DMSP-producing bacteria and the transcriptomes of many
512 eukaryotes, no homologue of *DsyB/DSYB/TpMMT* was detected. This indicates that
513 different isozymes or even DMSP biosynthesis pathways exist in these strains to be
514 further explored. As for DMSP degradation, no homologues of the known *Alma1* and
515 *ddd* DMSP lyase genes were detected in the transcriptomes of the DMSP-cleaving
516 eukaryote *Ulva* and the genomes of *Ddd*⁺ prokaryotic *Actinobacteria*, so novel DMSP
517 cleavage gene(s) still exist to be discovered.

518 Many marine bacteria (e.g., *L. aggregata* and *Pseudoceanicola batsensis*) and
519 algae (e.g., *E. huxleyi* and *Phaeocystis* sp.) not only make DMSP but also cleave this
520 compound (Stefels and Dijkhuizen, 1996; Alcolombri et al., 2015; Curson et al., 2017).
521 What are the endogenous and/or external incentives for this ability? What is its
522 physiological relevance? How are these contradictory processes being precisely
523 regulated in one organism? The functions of DMSP and DMS in marine organisms still
524 need to be verified at a molecular genetic level. These unanswered questions could be
525 the focus for our future in-depth studies on the molecular mechanisms of DMSP
526 biosynthesis and degradation, and their relevant functions in driving the global sulfur
527 cycle.

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Table 1 The distribution of DMS and DMSP in typical sea areas reported in the literature

Sea areas	Longitude	Latitude	Sampling time	Station numbers	T (°C)*	Sampling depth (m)	DMS (nM)	DMSPd (nM)	DMSPp (nM)	DMSPt (nM)	Reference
SAMPLING STATIONS WITH POINT RECORDS											
Western Mediterranean	0°00'E– 06°20'E	43°50'N– 38°00'N	1 Jun.–2 Aug., 1993 26–28 Apr. & 15–21 Jul., 1994	54	N.D.	0–200	0–19.3	0.1–18.3	N.D.	N.D.	Simo et al., 1997
Belgian Coastal Zone	02°30'E– 03°10'E	51°48'N– 51°18'N	Jan.–Dec., 2016	9	6.9–19.8	3	0–269.7	N.D.–39.3	N.D.– 1740.0	N.D.– 1779.3§	Speeckaert et al., 2018
The northern North Sea	02°30'E– 03°33'E	58°52'N– 58°15'N	18–28 Jun., 1999	8	11.2–12.3	5–11	3.7–10.1	54.0– 121.0	4.4–16.4	58.4–137.4§	Archer et al., 2001
The Gulf of Lion (the Mediterranean Sea)	03°40'E	42°20'N	Apr., 1990	N.D.	N.D.	15	9.24–14.3 (DMS+DMSPd)		31.9–39.0	N.D.	Belviso et al., 1993
The Central Ligurian Sea (the Mediterranean Sea)	07°52'E	43°24'N	16–22 May, 1990	N.D.	N.D.	15	4.19–5.01	2.8–6.8	24.8–30.2	~32.3§	Belviso et al., 1993
North Aegean Sea (Greece)	24°51'E– 25°52'E	40°51'N– 39°41'N	Sep., 2003	11	15.8–25.2	0–20	N.D.	11.6–19.4	N.D.	16.4–30.0	Mara et al., 2015
	24°03'E– 25°52'E	40°51'N– 39°41'N	Jul., 2004	10	14.6–24.5	0–20	N.D.	8.4–20.2	N.D.	15.4–31.4	Mara et al., 2015
Barents Sea (Russia)	30°21'E– 32°56'E	76°32'N– 72°45'N	13–29 May, 1993	4	N.D.	20–200	2.8–25.3	4.0–36.0	6.0–27.0	10.0–63.0§	Matrai et al., 1997
Western Indian Ocean	50°00'E– 77°00'E	24°00'S– 49°00'S	3–20 Dec., 1997	N.D.	N.D.	8	0.9–35.8	N.D.	N.D.	N.D.	Sciare et al., 1999
The Southern Ocean (Australasian sector)	60°00'E– 160°00'E	70°00'S– 40°00'S	25 Sep., 1991–8 Dec., 1995	N.D.	N.D.	0–4441	nd–22.0	nd–71.0	nd–102.0	nd–173.0§	Curran et al., 1998
The Southern Ocean (Indian sector)	71°00'E– 79°00'E	49°00'S– 53°50'S	19 Jan.–13 Feb., 2005	18	3	0–150	0.2–0.8	N.D.	5.0–20.0	N.D.	Belviso et al., 2008
Indian Estuaries (India)	72°00'E– 88°00'E	23°00'N– 09°00'N	28 Jul.–18 Aug., 2011 & 2–15 Jan., 2012	25	N.D.	0-5	0.1–38.3	N.D.	N.D.	N.D.	Viswanadham et al., 2016

Coastal Bay of Bengal (Northeastern part of the Indian Ocean)	81°00'E– 87°40'E	20°20'N– 15°30'N	23 Jul.–10 Aug., 2010	71	26.8–29.9	N.D.	1.2–28.2	N.D.	N.D.	0.8–61.6	Rao et al., 2015
Bohai Sea and Northern Yellow Sea (China)	112°00'E– 124°06'E	39°29'N– 17°43'N	21 Nov.–1 Dec., 2011	40	10.49– 15.77	16–77	0.8–6.7	0.9–12.9	7.6–42.3	9.0–45.2§	Yang et al., 2015
South China Sea (China)	113°50'E– 119°08'E	17°00'N– 14°00'N	20 May–17 Jul., 2014	19	29.25– 30.66	1020–5112	0.2–4.3	0.1–3.3	0.1–6.9	1.0–7.9	Zhai et al., 2018
Antarctic Sea Ice	115°00'E– 125°00'E	64°00'S– 66°00'S	27 Sep.–31 Oct., 2012	18	-22– -3.6	0.14–1.5	N.D.	N.D.	N.D.	0.5–750.0	Damm et al., 2016
Yellow Sea and East China Sea	119°50'E– 128°59'E	38°48'N– 25°41'N	26 Apr.–21 May, 2009	64	10–26	15–946	1.2–12.6	N.D.	N.D.	5.5–73.7	Yang et al., 2012
Yellow Sea and East China Sea	119°57.840' E– 127°16.29 1'E	34°59.924' N– 25°11.064' N	28 Jun.–15 Jul., 2006 22 Jan.–13 Feb., 2007	35 (summer), 53 (winter)	17.9–29.6 (summer) 6.3–24.0 (winter)	1.6–2.7 (summer) 15–1770 (winter)	1.8–12.2 (summer) 1.0–3.5 (winter)	N.D. (summer) N.D. (winter)	N.D. (summer) 14.0–45.0 (summer) 6.5–18.0 (winter)	14.0–45.0 (summer) 6.5–18.0 (winter)	Yang et al., 2011
Jiaozhou Bay (China)	120.18°E– 120.91°E	36.12°N– 35.80°N	19–21 May., 2006	14	N.D.	0.2	2.6–7.7	6.3–27.6	7.2–31.5	13.5–59.1§	Zhang et al. 2010
Yellow Sea (China)	121°00'E– 124°00'E	39°00'N– 33°00'N	Mar., 2005	21	2.81–9.50	19–75	0.99–5.10	2.13–13.3	4.89–40.1	N.D.	Yang et al., 2006
Yellow Sea (China)	121°14'E– 124°00'E	39°10'N– 32°30'N	Apr., 2006	43	4.5–13.74	20–88.5	1.7–12.8	2.9–38.8	4.3–36.1	7.2–74.9§	Zhang et al., 2008
East Yellow Sea and South China Sea (China)	121°22'E– 127°19'E	36°54'N– 27°30'N	5–26 Jul., 2011	60	17.85– 28.62	20.7–1377	0.6–41.2	1.4–27.2	6.2–207.7	7.6–234.9	Zhang et al., 2014
East China Sea (China)	121°40'E– 127°20'E	31°83'N– 26°20'N	19 Oct.–2 Nov., 2015	22	19.7–25.9	31–1014	1.0–9.6	1.7–7.2	5.6–83.8	7.4–91.0§	Zhang et al., 2017
Chang Jiang River Estuary (China)	122°00'E– 124°30'E	33°20'N– 27°50'N	7–14 Jun., 2014	32	19.67– 24.86	SW	2.2–27.5	N.D.	N.D.	5.9–195.0	Tan et al., 2017
Maizuru Bay (Japan)	135°20'E	35°27'N	May, 1986–Apr., 1987	5	N.D.	N.D.	0.64–289.7	N.D.	N.D.	N.D.	Uchida et al., 1992
Funka Bay (Japan)	140°50'E– 141°00'E	42°60'N– 42°00'N	23 Oct., 2000–9 Mar., 2001	28	1.11–16.16	SM & SW	N.D.	2.1–48.6	3.8–202.6	19.7–300.7§	Yang et al., 2005

The Subarctic North Pacific	148°00'E– 140°00'W	57°40'N– 42°00'N	14 Jul.–5 Sep., 1997	21	N.D.	10–100	1.3–13.2	N.D.	N.D.	N.D.	Aranami et al., 2001
Ross Sea (the bay of Southern Ocean in Antarctica)	167°00'E– 179°10'W	74°50'S– 78°00'S	31 Dec., 2004–21 Jan., 2005 & 10–30 Nov., 2005	8	-2.1–1.6	390–740	0.1–23.0	N.D.	N.D.	0.5–78.0	Rellinger et al., 2009
The Southern Ocean (Near south of New Zealand)	170°00'E– 180°00'E	49°00'S– 76°50'S	31 Oct.–16 Nov., 2003 & 20–28 Dec., 2004 & 28 Oct.–8 Nov., 2005	>55	0–7	4	0.6–30.0	N.D.	N.D.	1.0–118.0	Kiene et al., 2007
North Pacific Ocean	177°48'E– 146°31'W	23°06'N– 08°25'N	12–28 Dec., 2011 & 16–18 Feb., 2012	8	25.35– 26.82	5	3.2–5.3	0.5–1.0	6.0–8.8	7.0–9.5	Cui et al., 2015
Northeast Pacific Ocean	126°10'W– 124°10'W	48°40'N– 44°50'N	14–18 May, 1985	N.D.	20	N.D.	0.6–2.8	N.D.	N.D.	N.D.	Andreae et al., 1988
Equatorial Pacific Ocean	124°39'W– 115°00'W	0°30'N– 0°00'S	7–10 Feb., 2012	5	23.86– 26.73	5	2.4–5.8	2.1–6.8	14.8–20.2	21.6–25.2	Cui et al., 2015
South Pacific Ocean	120°00'W– 84°52'W	14°45'S– 22°31'S	6–24 Jan., 2012	7	24.04– 25.82	5	3.2–6.3	N.D.	N.D.	N.D.	Cui et al., 2015
Amundsen Sea	118°00'W– 101°40'W	70°20'S– 74°57'S	11 Jan.–16 Feb., 2009	51	-1.8–1.9	9–160	<1–350	N.D.	N.D.	N.D.	Tortell et al., 2012
Canadian Subarctic and Arctic Marine	100.69°W– 53.37°W	74.75°N– 56.12°N	10 Jul.–20 Aug., 2015.	9	-2–8	2.1–41.4	~1.0–18.0	N.D.	N.D.	10.6–38.2	Jarníková et al., 2018
Northern Gulf of Mexico (American)	92°00'W– 89°00'W	30°00'N– 26°00'N	12–21 Sep., 2011	12	27.3–29.2	1.4–30.6	0.8–4.7	0.8–2.9	5.9–27.3	8.6–29.0	Motard-Côté et al., 2016
Northern Baffin Bay (Lancaster Sound), Canadian	90°00'W– 64°50'W	77°30'N– 70°50'N	7–27 Sep., 2008	14	-1.3–3.8	2–4	0.5–4.8	0–2.1	5.0–70.0	5.5-71.7§	Motard-Côté et al., 2012
Ochlockonee Bay (America)	84°28'W– 84°15'W	30°00'N– 29°56'N	Sep., 1986	12	N.D.	3	1.8–14.0	2.0–22.5	4.0–42.0	6.0–57.0 §	Iverson et al., 1989
Chesapeake Bay (including the Potomac River) (USA)	77°20'W– 75°00'W	39°00'N– 33°00'N	Sep., 1986	>60	N.D.	3	1.0–18.0	0–18.0	1.0–64.0	1.0–68.0	Iverson et al., 1989
Long Island Sound estuary (America)	72°06'W–	41°20'N–	Dec., 1998–Jan., 2000	3	2–25	0	0–3.0	0–3.0	1.0–49.0	1.0–52.0	Tang et al., 2000

	72°04'W	41°18'N										
Marguerite Bay (West Antarctic Peninsula)	71°20'W–68°10'W	66°50'S–68°30'S	1–7 Jan., 2015	11	-1–0.5	5–129	N.D.	12.0–275.0§	82.0–368.0	94.0–643.0	Stefels et al., 2018	
Gulf of Maine (Canada)	69°30'W–68°20'W	43°10'N–41°00'N	Jul., 1990	7	N.D.	0–100	0.8–8.3	0–175.0	0–260.0	1.3–368.0	Matrai et al., 1993	
Sargasso Sea (North Atlantic Ocean)	64°30'W	32°10'N	Jan., 1992–Dec., 1993	1	N.D.	0–140	0–12.0	0–20.0	0–27.0	0–47.0§	Dacey et al., 1998	
Northwest Atlantic	62°17'W–41°00'W	61°22'N–38°00'N	10 Sep.–2 Oct., 1999	8	2.8–27.4	6.3–7.4	0.2–7.7	1.9–54.3	7.3–119.8	10.1–203.0	Scarratt et al., 2007 & Yang et al., 2009	
Gulf of Saint Lawrence (Canada)	60°00'W–64°00'W	49°00'N–47°00'N	4–11 Aug., 1993	79	13–19	0–100	0–8.8	1.7–23.1	6.1–117.0	7.8–140.1§	Cantin et al., 1996	
Atlantic Ocean	60°00'W–00°00'W	40°00'S–50°00'N	Mar.–Apr., 1987	28	N.D.	10	0.1–10.0	N.D.	N.D.	0–23.0	Burgermeister et al., 1990	
Western North Atlantic	57°41.2'W–45°00'W	59°14.7'N–36°49.5'N	8–22 July, 2003	8	4.08–26.14	1	0.2–7.6	1.87–54.3	7.3–119.8	N.D.	Yang et al., 2009	
Antarctic Ocean	54°00'W–87°00'W	52°00'S–71°00'S	24 Oct.–29 Dec., 1992	>123	-1.4–0.9	3	0.2–27.0	1.0–28.0	2.0–69.0	N.D.	Turner et al., 1995	
The tropical Northeastern Atlantic Ocean	31°00'W	21°00'N	21–22 Sep., 1991 & 14 Oct., 1991	3	N.D.	0–150	0.5–2.2	2.0–14.4§	0–37.0	2.0–40.4§	Belviso et al., 1993	
	21°00'W	18°30'N	16–17 Sep., 1991	2	N.D.	0–100	0.6–2.5	1.0–9.3§	0–39.0	1.9–45.5§		
	21°00'W	18°30'N	6–7 Oct., 1991	3	N.D.	0–100	2.3–7.6	0–2.3§	12.5–37.5	14.8–18.2§		
Northeast Atlantic (between UK and Iceland)	21°00'W–0°00'W	65°00'N–54°00'N	Jun.–Jul., 1987	158	N.D.	3	1.1–93.8	<1.3–199.0	10.8–280.0	12.1–479.0§	Malin et al., 1993	
The Western Coast of Ireland	15°00'W–10°00'W	55°00'N–51°00'N	26 Jun.–2 Jul., 1996	>350	N.D.	3–200	<0.2–42.0	20.0–80.0	50.0–635.0	N.D.	Locarnini et al., 1998	
Mediterranean Sea	10°00'W–22°00'E	38°00'N–30°50'N	11–20 Sep., 1999	>61	N.D.	3–5	0.4–90.0	N.D.	N.D.	20.0–300.0	Belviso et al., 2003	
Norwegian and Greenland Seas	08°00'W–10°00'E	75°00'N–66°00'N	Jul.–Sep., 2012	17	5.74–11.64	0–4000	0.8–22.4	0.4–43.3	0.1–282.4	N.D.	Li et al., 2015	
Southern Ocean (Atlantic)	06°00'W	60°00'S	29 Sep.–26 Nov.,	13	N.D.	20	N.D.	3.0–66.0	3.0–61.0	6.0–127.0§	Deyerdierks et al., 1997	

sector)		47°00'S		1992							
SAMPLING STATIONS WITH DEPTH-PROFILE											
The Southern Ocean (Australasia sector)	60°00'E–160°00'E	70°00'S–40°00'S	25 Sep.,1991–8 Dec.,1995	N.D.	N.D.	0–1000	0.7–3.2	N.D.	N.D.	0.7–2.4	Curran et al., 1998
						3000–4000	1.1–4.0	N.D.	N.D.	N.D.	
						4000–4441	0.3–4.5	N.D.	N.D.	N.D.	
South China Sea	113°50'E–119°08'E	17°00'N–14°00'N	20 May–17 Jul., 2014	19	29.25–30.64	1020–3000	0.3–3.5	0.1–3.3	1.1–5.9	1.2–9.2§	Zhai et al., 2018
						3000–4000	0.2–1.5	0.2–0.8	1.0–3.2	1.20–4.0§	
						4000–5112	0.2–4.3	0.1–1.5	0.1–6.9	0.3–8.4§	
East China Sea and Yellow Sea	119°58'E–128°37'E	35°00'N–25°11'N	22 Jan.–13 Feb. 2007	53	6.3–24	15–100	1.3–3.5 (2.0)	N.D.	N.D.	7.1–18.0 (12.1)	Yang et al., 2011
						100–200	1.1–2.6 (1.8)	N.D.	N.D.	6.52–14.28 (10.8)	
						400–500	1.2	N.D.	N.D.	9.0	
						500–600	1.2	N.D.	N.D.	6.7	
						600–700	1.0	N.D.	N.D.	6.9	
						700–800	1.4	N.D.	N.D.	9.0	
						800–900	1.2–1.4 (1.3)	N.D.	N.D.	7.3–8.7 (8.0)	
						1000–1500	1.3	N.D.	N.D.	7.6	
						1500–2000	1.2	N.D.	N.D.	7.4	
Norwegian and Greenland Seas	05°00'W–10°00'E	75°00'N–66°00'N	Jul.–Sep., 2012	17	0.0–7.5	0–1000	0.5–10.0	0.5–20.0	5–130.0§	5.0–150.0	Li et al., 2015
						1000–2000	0.5–3.0	0–8.0	0–12.0§	0–20.0	
						2000–3000	0.5–5.0	0–15.0	0–5.0§	0–20.0	
						3000–4000	0–3.0	0–2.0	0–10.0§	0–10.0	

* Surface (0–1 m) seawater temperature. § values from calculation. N.D., no data. nd, nondetectable. SW, surface water; SM, surface microlayer.

Table 2 Major representative DMSP-producing biological taxa

Taxonomic position (phylum/class/family)	Species or Strain	Biosynthesis Pathway	Key Enzyme & Peptide type	Intracellular DMSP Concentration (mM)*	DMSP Production*	Reference
ALGAE AND CORALS (EUKARYOTE)						
Haptophyta/Prymnesiophyceae/Chrysochromulinaceae	<i>Chrysochromulina tobin</i> CCMP291	Transamination	DSYB; MTHB methyltransferase	0.611 ± 0.08	N.T.	Curson et al., 2018
	<i>Chrysochromulina</i> sp. PCC307	Transamination	DSYB; MTHB methyltransferase	0.196 ± 0.0394	N.T.	Curson et al., 2018
Haptophyta/Prymnesiophyceae/Prymnesiaceae	<i>Prymnesium parvum</i> CCAP946/6	Transamination	DSYB; MTHB methyltransferase	54.3 ± 5.97	N.T.	Curson et al., 2018
	<i>Prymnesium parvum</i> CCAP941/6	Transamination	DSYB; MTHB methyltransferase	20.6 ± 3.05	N.T.	Curson et al., 2018
	<i>Prymnesium parvum</i> CCAP946/1A	Transamination	DSYB; MTHB methyltransferase	53.8 ± 4.58	N.T.	Curson et al., 2018
	<i>Prymnesium parvum</i> CCAP946/1D	Transamination	DSYB; MTHB methyltransferase	35.5 ± 1.50	N.T.	Curson et al., 2018
	<i>Prymnesium parvum</i> CCAP946/1B	Transamination	DSYB; MTHB methyltransferase	48.4 ± 6.29	N.T.	Curson et al., 2018
	<i>Prymnesium patelliferum</i> CCAP946/4	Transamination	DSYB; MTHB methyltransferase	25.3 ± 2.39	N.T.	Curson et al., 2018
	Haptophyta/Prymnesiophyceae/Hymenomonadaceae	<i>Hymenomonas carterae</i>	Unknown	Unknown	120	N.T.
Haptophyta/Prymnesiophyceae/Phaeocystaceae	<i>Phaeocystis</i> sp.	Unknown	Unknown	71–169	N.T.	Stefels and van Boekel, 1993
Haptophyta/Chrysophyceae/Chromulinaceae	<i>Ochromonas</i> sp.	Unknown	Unknown	529	N.T.	Keller et al., 1989

Haptophyta/Coccolithophyceae/Noelaerhabdaceae	<i>Emiliana huxleyi</i> BT6	Unknown	Unknown	166	N.T.	Keller et al., 1989
Bacillariophyta/Bacillariophyceae/Bacillariaceae	<i>Fragilariopsis cylindrus</i> CCMP1102	Transamination	DSYB; MTHB methyltransferase	6.71 ± 0.92	N.T.	Lyon et al., 2011; Curson et al., 2018
Bacillariophyta/Coscinodiscophyceae/Thalassiosiraceae	<i>Thalassiosira pseudonana</i>	Transamination	TpMMT; MTHB methyltransferase	~20–30	~1 µmol/g fresh mass	Kageyama et al., 2018; Kettles et al., 2014
Bacillariophyta/Coscinodiscophyceae/Melosiraceae	<i>Melosira numuloides</i>	Unknown	Unknown	264	N.T.	Keller et al., 1989
Dinophyta/Dinophyceae/Symbiodiniaceae	<i>Symbiodinium microadriaticum</i> CCMP2467	Transamination	DSYB; MTHB methyltransferase	282 ± 35.0	N.T.	Curson et al., 2018
Dinophyta/Dinophyceae/Cryptothecodiniaceae	<i>Cryptothecodinium cohnii</i> ATCC e32001	Decarboxylation	Unknown; L-Met decarboxylase	N.T.	10 ² –10 ³ µg/L culture	Uchida et al., 1993 & 1996; Kitaguchi et al., 2008
Dinophyta/Dinophyceae/Gymnodiniaceae	<i>Gymnodinium nelsonii</i>	Unknown	Unknown	280	N.T.	Dacey and Wakeham, 1986
Dinophyta/Dinophyceae/Prorocentraceae	<i>Prorocentrum</i> sp. IIB2b1	Unknown	Unknown	1,082	N.T.	Curson et al., 2018
Chlorophyta/Chlorophyceae/Volvocaceae	<i>Platymonas subcordiformis</i>	Unknown	Unknown	170	N.T.	Dickson and Kirst, 1986
Chlorophyta/Ulvophyceae/Ulvaceae	<i>Ulva lactuca</i>	Unknown	Unknown	N.T.	23–128 mmol/g fresh mass	Greene, 1962; Reed, 1983; Van Alstyne et al., 2007
	<i>Ulva intestinalis</i>	Transamination	Unknown; D-MTHB S-Methyltransferase	N.T.	7–34 mmol/g fresh mass	Gage et al., 1997; Reed, 1983; Van Alstyne et al., 2001; Summers et al., 1998

	<i>Ulva pertusa</i>	Transamination	Unknown; MTHB S- methyltransferase	N.T.	~12–37 µmol/g fresh mass	Ito et al., 2011
Rhodophyta/Florideophyceae/Hypneaceae	<i>Hypnea spinella</i>	Unknown	Unknown	N.T.	0.02–0.2 mmol/g fresh mass	Bischoff et al., 1994
Rhodophyta/Florideophyceae/Rhodomelaceae	<i>Polysiphonia fastigiata</i> & <i>Polysiphonia nigrescens</i>	Unknown	Unknown	N.T.	N.T.	Challenger and Simpson, 1948
	<i>Polysiphonia hendryi</i>	Unknown	Unknown	N.T.	8–30 mmol/g fresh mass	Van Alstyne et al., 2001
	<i>Polysiphonia lanosa</i>	Unknown	Unknown	N.T.	45–97 mmol/g fresh mass	Reed, 1983
	<i>Rhodomela confervoides</i>	Unknown	Unknown	N.T.	4–8 mmol/g fresh mass	Reed, 1983
	<i>Chondria coerulescens</i>	Unknown	Unknown	N.T.	N.T.	Chillemi et al., 1990
Streptophyta/Liliopsida/Poaceae	<i>Spartina alterniflora</i>	Methylation	Unknown; L-Met methyltransferase	N.T.	29.0 µmol/g fresh mass	Kocsis et al., 1998
	<i>Saccharum</i> spp. (sugarcane)	Unknown	Unknown	N.T.	6 µmol/g fresh mass	Paquet et al., 1994
Streptophyta/-/Asteraceae	<i>Wollastonia biflora</i>	Methylation	Unknown; L-Met methyltransferase	N.T.	~12–30 µmol/g fresh mass	Hanson et al., 1994; James et al., 1995
Cnidaria/Anthozoa/Acroporidae	<i>Acropora cervicornis</i>	Transamination	DSYB; MTHB methyltransferase	N.T.	N.T.	Curson et al., 2018

<i>Acropora millepora</i>	Transamination	Unknown	N.T.	~2.5–5.2 nmol/mm ²	Raina et al., 2013
<i>Acropora tenuis</i>	Transamination	Unknown	N.T.	~3.1–6.0 nmol/mm ²	Raina et al., 2013

BACTERIA (PROKARYOTE)

Proteobacteria/Alphaproteobacteria/Rhodobacteraceae	<i>Pseudoceanicola batsensis</i> HTCC2597	Transamination	DsyB; MTHB methyltransferase	6.3	40.5 ± 0.2 pmol/μg protein	Curson et al, 2017
	<i>Pelagibaca bermudensis</i> HTCC2601	Transamination	DsyB; MTHB methyltransferase	40.6	259 ± 52.7 pmol/μg protein	Curson et al, 2017
	<i>Sediminimonas qiaohouensis</i> DSM21189	Transamination	DsyB; MTHB methyltransferase	19.1	122 ± 4.6 pmol/μg protein	Curson et al, 2017
	<i>Sagittula stellata</i> E-37	Transamination	DsyB; MTHB methyltransferase	1.7	11.1 ± 0.3 pmol/μg protein	Curson et al, 2017
Proteobacteria/Alphaproteobacteria/Stappia_f	<i>Labrenzia aggregata</i> LZB033	Transamination	DsyB; MTHB methyltransferase	9.6	99.8 ± 1.2 pmol/μg protein	Curson et al, 2017
	<i>Labrenzia aggregata</i> IAM 12614	Transamination	DsyB; MTHB methyltransferase	5.1	32.9 ± 2.7 pmol/μg protein	Curson et al, 2017
Proteobacteria/Alphaproteobacteria/Rhodobiaceae	<i>Amorphus coralli</i> DSM19760	Transamination	DsyB; MTHB methyltransferase	1.3	8.2 ± 0.2 pmol/μg protein	Curson et al, 2017

Proteobacteria/Alphaproteobacteria/Rhodospirillaceae	<i>Thalassobaculum salexigens</i> DSM19539	Transamination	DsyB; MTHB methyltransferase	0.8	4.8 ± 1.6 pmol/μg protein	Curson et al, 2017
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*Values that were taken from the literature with various incubation conditions and culturing media. # Per liter of cell volume. N.T., not tested.

Table 3 Major representative DMSP-degrading biological taxa

Taxonomic position (phylum/class/family)	Strain	Degradation enzyme	DMSP breakdown product	Polypeptide class	Crystallization, co-factor and key amino acid residue	Reference
BACTERIA (PROKARYOTE)						
Proteobacteria/Alphaproteobacteria/Rhodobacteraceae	<i>Roseobacter sp.</i> MED193	DddW	DMS and acrylate	cupin superfamily	no	Todd et al., 2012a
	<i>Ruegeria pomeroyi</i> DSS-3	DddW	DMS and acrylate	cupin superfamily	no	Todd et al., 2012a Brummett et al., 2015
		DddQ	DMS and acrylate	cupin superfamily	no	Todd et al., 2011
		DddP	DMS and acrylate	M24B metallopeptidase family (COG0006)	no	Curson et al., 2011a
		DmdA	MMPA plus X-CH ₃ (in which X is tetrahydrofolate)	Glycine cleavage system T family (COG0404)	no	Reisch et al., 2008
	<i>Ruegeria lacuscaerulensis</i> ITI_1157	DddQ	DMS and acrylate	cupin superfamily	yes, Zn ²⁺ , Tyr131 or Fe ³⁺ , Tyr120	Li et al., 2014 Curson et al., 2011b; Brummett et al., 2016
	<i>Roseobacter denitrificans</i>	DddP	DMS and acrylate	M24B metallopeptidase family (COG0006)	yes, Fe ³⁺	Hehemann et al., 2014
	<i>Ruegeria lacuscaerulensis</i>	DddP	DMS and acrylate	M24B metallopeptidase family (COG0006)	yes, Zn ²⁺ ,	Wang et al., 2015
	<i>Roseovarius nubinhibens</i> ISM	DddQ	DMS and acrylate	cupin superfamily	no	Kirkwood et al., 2010
		DddP	DMS and acrylate	M24B metallopeptidase family (COG0006)	no	Todd et al., 2009
	<i>Sagittula stellata</i> E-37	DddD	DMS and 3HP	Class III CoA transferase family (COG1804)	no	Curson et al., 2011a
	<i>Dinoroseobacter shibae</i> DFL 12	DddL	DMS and acrylate	cupin superfamily	no	Curson et al., 2011a
	<i>Sulfitobacter sp.</i> EE-36	DddL	DMS and acrylate	cupin superfamily	no	Curson et al., 2011a
Proteobacteria/Alphaproteobacteria/Alcaligenaceae	<i>Alcaligenes faecalis</i> M3A	DddY	DMS and acrylate	cupin superfamily	no	Curson et al., 2011b
Proteobacteria/Alphaproteobacteria/Rhizobiaceae	<i>Rhizobium</i> NGR234	DddD	DMS and 3HP	Class III CoA transferase family (COG1804)	no	Todd et al., 2007

Proteobacteria/Alphaproteobacteria/Pelagibacteraceae	<i>Pelagibacter ubique</i>	DmdA	MMPA plus X-CH ₃ (in which X is tetrahydrofolate)	Glycine cleavage system T family (COG0404)	yes, THF used as methyl acceptor	Reisch et al., 2008
		DddK	DMS and 3HP	cupin superfamily	yes, Fe ²⁺ Zn ²⁺ , Tyr64	Schnicker et al., 2017
Proteobacteria/Gammaproteobacteria/Oceanospirillaceae	<i>Marinomonas</i> MWYL1	DddD	DMS and 3HP	Class III CoA transferase family (COG1804)	no	Todd et al., 2007
Proteobacteria/Gammaproteobacteria/Moraxellaceae	<i>Acinetobacter bereziniae</i>	DddY	DMS and acrylate	cupin superfamily	yes, Zn ²⁺ , Tyr271	Li et al., 2017
Proteobacteria/Gammaproteobacteria/Shewanellaceae	<i>Shewanella putrefaciens</i> CN-32	DddY	DMS and acrylate	cupin superfamily	no	Curson et al., 2011b; Lei et al., 2018
Proteobacteria/Gammaproteobacteria/Halomonadaceae	<i>Halomonas</i> HTNK1	DddD	DMS and 3HP	Class III CoA transferase family	no	Todd et al., 2010
Proteobacteria/Betaproteobacteria/Burkholderiaceae	<i>Burkholderia cepacia</i> AMMD	DddD	DMS and 3HP	Class III CoA transferase family (COG1804)	no	Todd et al., 2007
Proteobacteria/Epsilonproteobacteria/Campylobacteraceae	<i>Arcobacter nitrofigilis</i> DSM7299	DddY	DMS and acrylate	cupin superfamily	no	Curson et al., 2011b
Proteobacteria/Deltaproteobacteria/Desulfovibrionaceae	<i>Desulfovibrio acrylicus</i> sp.	DddY	DMS and acrylate	cupin superfamily	no	Van der Maarel and Hansen, 1996; Curson et al., 2011b
Actinobacteria/Actinobacteria/Nocardiaceae	<i>Rhodococcus</i> sp. DY1, DY5, DY6, DY7 & DY8	Unknown	DMS and acrylate/3HP	N.A.	N.A.	Yoch et al., 2001
Firmicutes/Clostridia/Clostridiaceae	<i>Clostridium</i> sp.	Unknown	DMS and acrylate	N.A.	N.A.	Wagner and Stadtman, 1962
ALGAE & FUNGI (EUKARYOTE)						
Ascomycota/Eurotiomycetes/Trichocomaceae	<i>Aspergillus oryzae</i> RIB40	DddP	DMS and acrylate	M24B metallopeptidase family (COG0006)	no	Todd et al., 2009
Ascomycota/Sordariomycetes/Nectriaceae	<i>Fusarium graminearum</i> cc19	DddP	DMS and acrylate	M24B metallopeptidase family (COG0006)	no	Todd et al., 2009
	<i>Fusarium culmorum</i> Fu42	DddP	DMS and acrylate	M24B metallopeptidase family (COG0006)	no	Todd et al., 2009
Haptophyta/Prymnesiophyceae/Noelaerhabdaceae	<i>Emiliania huxleyi</i> HL373	Alma1	DMS and acrylate	aspartate racemase superfamily	no	Alcolombri et al., 2015

	<i>E. huxleyi</i> BT6	Unknown	DMS and acrylate	N.A.		N.A.	Yoch, 2002
Haptophyta/Prymnesiophyceae/Phaeocystaceae	<i>Phaeocystis</i> sp.	Unknown	DMS and acrylate	N.A.		N.A.	Stefels et al., 1995
Alveolata/Dinophyceae/Symbiodiniaceae	<i>Symbiodinium microadriaticum</i> ;	Unknown	DMS and acrylate	N.A.		N.A.	Yost and Mitchelmore, 2009
	<i>Symbiodinium</i> sp.	Alma1	DMS and acrylate	aspartate superfamily	racemase	no	Alcolombri et al., 2015
Alveolata/Dinophyceae/Thoracosphaeraceae	<i>Scrippsiella</i> spp.	Unknown	DMS and acrylate	N.A.		N.A.	Niki et al., 1997
Alveolata/Dinophyceae/Heterocapsa	<i>Heterocapsa triquetra</i> NIES-7	Unknown	DMS and acrylate	N.A.		N.A.	Niki et al., 2000
Chlorophyta/Ulvophyceae/Ulvaceae	<i>Ulva lactuca</i>	Unknown	DMS and acrylate	N.A.		N.A.	Diaz et al. 1994
Rhodophyta/Florideophyceae/Rhodomelaceae	<i>Polysiphonia paniculata</i>	Unknown	DMS	N.A.		N.A.	Nishiguchi and Goff, 2010
	<i>Polysiphonia lanosa</i>	Unknown	DMS and acrylate	N.A.		N.A.	Anderson and Cantoni, 1956

N.A. not applicable; MMPA, methylmercaptopropionate.

Table 4 Functions of DMSP and DMS

Compounds	Functional types	Specific functions	Related organisms	References
DMSP	Physiological functions	Osmoprotectant	<i>Poteroochromonas malhamensis</i> (Synurophyceae); <i>Dunaliella</i> spp. (Chlorophyceae); <i>Polysiphonia lanosa</i> (Florideophyceae); <i>Blidingia minima</i> (Ulvophyceae); <i>Ulva lactuca</i> (Ulvophyceae); some Rhodophyceae; some Phaeophyceae	Kirst, 1990; Vairavamurthy et al., 1985
		Cryoprotectant	<i>Acrosiphonia arcta</i> (Ulvophyceae); <i>Microcoleus chthonoplastes</i> (Cyanobacteria); <i>Enteromorpha bulbosa</i> (Ulvophyceae); <i>Ulothrix subflaecida</i> (Klebsormidiophyceae)	Karsten et al., 1996
		Antioxidant	<i>Phaeocystis</i> sp. (Haptophyceae); <i>Emiliana huxleyi</i> (Haptophyceae); <i>Prymnesium parvum</i> (Haptophyceae); <i>Thalassiosira pseudonana</i> (diatom); <i>Skeletonema costatum</i> (diatom); <i>Pfiesteria piscicida</i> (Dinophyceae)	Sunda et al., 2002; Lesser, 2006; Husband et al., 2012; Curson et al., 2018
		Sink of excess sulfur, carbon and reduced equivalent	photosynthetic marine algae and higher plants e.g. <i>Enteromorpha intestinalis</i> (Ulvophyceae)	Gage et al., 1997; Stefels 2000; Bullock et al., 2017

	Saving nitrogen for cell growth and accelerating sulfate uptake from the environment		
Biological functions	Resolving the damage of thermal stress and signal molecule attracting certain beneficial bacteria for coral	<i>Acropora millepora</i> and <i>Acropora tenuis</i> (coral);	Raina et al., 2013
	Predator deterrent	<i>Emiliana huxleyi</i> (Haptophyceae)	Wolfe and Steinke, 1996
	Mediator of bacterial virulence associated with regulation of <i>E. huxleyi</i> blooms	<i>Emiliana huxleyi</i> (Haptophyceae); <i>Sulfitobacter</i> (Alphaproteobacteria); <i>Pseudoalteromonas piscicida</i> (Gammaproteobacteria)	Barak-Gavish et al., 2018
	Chemoattractant	<i>Silicibacter</i> sp.(Alphaproteobacteria); reef fishes	Miller et al., 2004; Seymour et al., 2010; DeBose et al., 2008
	Bacterial quorum sensing inducer, related to decomposition of particulate organic matter (POC)	<i>Ruegeria pomeroyi</i> DSS-3 (Alphaproteobacteria)	Seyedsayamdost et al., 2011; Johnson et al., 2016
Ecological functions	The main precursor of DMS	N.A.	Stefels et al., 1993; Hill et al., 1998

		Biogeochemical cycle of sulfur and carbon in the ocean	N.A.	Curson et al., 2011a
DMS	Biological function	Chemoattractant	<i>Diomedea exulans</i> and <i>Pachyptila desolata</i> (Aves); fish over coral reefs; calanoid and <i>Temora longicornis</i> (copepod); Flagellates and ciliates;	Steinke et al., 2006; DeBose and Nevitt, 2008; Nevitt, 2008
		Antioxidant	<i>Emiliana huxleyi</i> (Haptophyceae) <i>Phaeocystis</i> sp. (Haptophyceae) <i>Skeletonema costatum</i> (Coscinodiscophyceae)	Sunda et al., 2002; Lesser, 2006
	Ecological functions	Climate-cooling gas, which is the precursor of sulfuric cloud condensation nuclei (CCN), increasing cloud formation and then the albedo of the earth	N.A.	Charlson et al., 1987; Ayers and Gras, 1991; Andreae and Crutzen, 1997
		The greatest flux of organosulfur from the ocean into the atmosphere	N.A.	Lovelock et al., 1972; Chin and Jacob 1996; Kettle and Andreae, 2000
		Ease the stratification of seawater and form a positive feedback loop	N.A.	Lovelock, 2006

N.A. not applicable.

Figure legends

Figure 1 The fate of dimethylsulfoniopropionate (DMSP) and dimethylsulfide (DMS). 3HP, 3-hydroxypropionate; CCN, cloud condensation nuclei; DMSO, dimethyl sulfoxide; MeSH, methanethiol; MMPA, methylmercaptopropionate; TCA, tricarboxylic acid; X, tetrahydrofolate.

Figure 2 Green tide outbreak in the beach of Qingdao, China in July 2018.

Figure 3 Predicted pathways for DMSP biosynthesis in higher plants, coral, phytoplankton and bacteria (modified from Curson et al., 2017).

Wollastonia (a), *Spartina* and bacteria (*Streptomyces*) (b); macroalgae (*Ulva*, *Enteromorpha*), diatoms (*Thalassiosira*, *Melosira*), prymnesiophyte (*Emiliana*), prasinophyte (*Tetraselmis*), coral (*Acropora*) and bacterium (*Labrenzia*) (c) and dinoflagellate (*Cryptocodinium*) (d).

Abbreviations: Met, methionine; AdoMet, S-adenosylmethionine; AdoHcy, S-adenosyl-L-homocysteine; DMSP-ald., DMSP-aldehyde; MMPA, methylmercaptopropionate.

Figure 4 Morphology of the model DMSP and DMS-producing bacterial strain *Labrenzia aggregata* LZB033. (A) Plate streaking of LZB033. (B) Fluorescence microscopy of LZB033 cells stained with DAPI. (C) Transmission electron microscopy of one LZB033 cell acquired from Marine Broth culture, scale bar = 1 μ m. (D) Transmission electron microscopy of transections and a longitudinal section of LZB033 cells processed by ultramicrotomy, scale bar = 500 nm.