nature reviews earth & environment

https://doi.org/10.1038/s43017-023-00428-7

Review article

The biogeochemistry of marine dimethylsulfide

Frances E. Hopkins[1], **Stephen D. Archer**[2], **Thomas G. Bell**[1], **Parvadha Suntharalingam**[3] & **Jonathan D. Todd**[4]

Abstract

The marine trace gas dimethylsulfide (DMS) supplies sulfur to the atmosphere at a rate of 15–40 Tg S per year, contributing to the production of atmospheric sulfate aerosols that influence cloud radiative properties and thereby climate. The resulting climate cooling effect of DMS is an estimated −1.7 to −2.3 W m^{-2}, which is similar in magnitude to the warming effect of anthropogenic CO_2 emissions (1.83 ± 0.2 W m^{-2}). In this Review, we describe the production and cycling of marine DMS and its fate in the atmosphere. Advances in molecular genetics and large-scale biogeochemical measurements have revealed the global prevalence of DMS-related processes, including in previously overlooked environments and organisms, such as sediment-dwelling bacteria. Most marine DMS (>90%) is degraded or consumed in the water column, but the remainder is emitted to the atmosphere, where it contributes to the formation of cloud condensation nuclei. Large uncertainties (up to ±10 W m^{-2}) associated with the global impact of DMS emissions arise from the use of crudely defined biological parameters, such as total chlorophyll, in models. Constraining and modelling the biogeochemical processes that control DMS production are key to better estimating the influence of DMS on climate.

Sections

[1]Plymouth Marine Laboratory, Plymouth, UK. [2]Bigelow Laboratory for Ocean Sciences, Boothbay, ME, USA. [3]School of Environmental Sciences, University of East Anglia, Norwich, UK. [4]School of Biological Sciences, University of East Anglia, Norwich, UK. ✉e-mail: fhop@pml.ac.uk

Introduction

The surface oceans are a major source of the marine trace gas dimethylsulfide (DMS), a volatile organic compound that can influence the formation of marine aerosols and impact cloud albedo and global radiative forcing[1–3]. Early DMS-related research was motivated by interest in the distinctive smell of the sea (which is mainly attributable to DMS), but the CLAW hypothesis[1,4] proposed in the 1980s attracted broader scientific attention to the role of DMS (Fig. 1). This hypothesis describes the theoretical biological regulation of climate via DMS emissions from marine phytoplankton, as DMS leads to the formation of cloud condensation nuclei (CCN), thereby influencing cloud albedo. The CLAW idea also speculated on the existence of a negative climatic feedback, whereby the rate of DMS emission from the ocean is affected by the climate, which in turn alters the biological production of DMS.

The proposal of CLAW drove more than 30 years of research motivated by the prospect of finding evidence of a biologically driven climate thermostat (reviewed elsewhere[5]). Some satellite-based evidence emerged of new particle formation from biological sources, with enhanced cloud droplet number over productive ocean regions[6]. However, overall the observational evidence was scant[7,8] and model results suggested low sensitivity of DMS–climate feedbacks[9,10]. As a result, a call was made to retire the CLAW hypothesis – and the idea that DMS functions as a biological climate feedback loop – in 2011 (ref. 11).

Nevertheless, interdisciplinary field research (Mace Head, Ireland, 2015 (ref. 12); Southern Ocean Clouds Radiation and Aerosol Transport Experimental Study (SOCRATES)[13]; Western Atlantic Climate Study 2 (WACS2) and the NASA North Atlantic Aerosols and Marine Ecosystems Study (NAAMES)[14–16]) has since demonstrated that aerosol distributions and CCN formation are tightly driven by biological production of DMS over some regions of the surface ocean. Furthermore, marine DMS emissions have a substantial impact on aerosol–cloud processes and global climate regulation[17,18]. The rapid oxidation of DMS in the atmosphere (the atmospheric lifetime of DMS is ~1.2 days[19,20]) leads to the formation of aerosols that influence the radiative balance of the Earth by scattering solar radiation and acting as CCN. The aerosol radiative forcing effect of these aerosols is estimated to be between −1.7 and −2.3 W m^{-2} (refs. 2,3,18,21), a similar magnitude to the positive forcing effect from anthropogenic CO_2 emissions (1.83 ± 0.2 W m^{-2})[22]. However, the DMS forcing estimate is associated with a much higher degree of uncertainty (up to ±10 W m^{-2}), partly driven by highly heterogeneous seasonal and spatial variability in DMS fluxes. This level of uncertainty highlights the need to better constrain surface ocean DMS concentrations, cycling and fluxes on regional scales[2,23–25].

In this Review, we describe the microbial pathways controlling dimethylsulfoniopropionate (DMSP) and DMS production and degradation. We discuss the role of DMS in atmospheric chemistry and global radiative forcing. Finally, we end with an assessment of future research priorities, including the need to unravel the key biological processes controlling DMS production to improve the accuracy of global DMS flux estimates and climate models. We provide recommendations for observational, experimental and modelling work on the effects of climate change stressors on DMS production and flux that are required to facilitate improved understanding of the role of DMS in the future climate.

Marine DMS production and cycling

DMS occurs in the nanomolar concentration range in seawater (generally 1–7 nM globally[23]). Most of this DMS is broken down through bacterial and light-driven processes[26,27], but the rest (<10% of the total loss) transfers across the sea–air interface. This flux represents the greatest natural source of sulfur from the oceans to the atmosphere (15–40 Tg S per year)[23,25] and is the main pathway from the marine to the terrestrial realm[28]. This section describes the biogeochemical pathways and molecular machinery driving net DMS production and discusses how omics data sets can be used to infer potential DMSP and DMS production, identify the key protagonists and predict hotspots of production.

DMSP sources

DMS production is ultimately driven by the availability of DMSP and its breakdown by bacterial and algal lyase enzymes[29,30] (Fig. 2). The dominant source of DMSP is direct biosynthesis, largely by autotrophic plankton in the marine photic zone, estimated to comprise >3.8 Pg C per year (perhaps up to 7.0 Pg C per year) and around 5–9% of the total carbon produced by marine primary production[31]. Notably, the haptophyte *Phaeocystis* sp. adopts growth strategies that lead to bloom formation, resulting in DMSP concentrations in seawater that can exceed 1 µM[32,33]. Unprecedented concentrations in excess of 4 µM were reported within a massive dinoflagellate bloom (*Akashiwo sanguinea*) at Monterey Bay, CA, USA[34]. However, such concentrations are considered rare or transient, with only 3 out of 4,600 data points from the global DMSP database (https://saga.pmel.noaa.gov/dms/) at or above 1 µM[31]. The photic layers are key in marine DMSP production, but the potential for marine sediment-dwelling organisms to synthesize substantial quantities of DMSP is becoming increasingly clear. For example, coastal surface sediments from saltmarsh ponds and estuaries contain abundant DMSP-producing organisms, including microphytobenthic diatoms and bacteria[35,36]. Aphotic and anoxic marine sediments, including those in the deep ocean[37], also can possess high levels of DMSP and bacteria with the potential to generate DMS (Fig. 3). DMSP is also produced profusely by ice algae, enabling them to tolerate hypersaline and low-temperature environments[38], and by coral symbionts[39–43], macroalgae[41,44] and saltmarsh plants such as *Spartina* spp.[45,46]. The global distribution of such organisms and environments is limited relative to phytoplanktonic DMSP sources in the Earth's ocean, so they are less important for global sulfur cycling and climate regulation[47] (Fig. 3).

DMSP production is thought to be driven by a metabolic incentive to protect the cell or organism from environmental fluctuations in salinity, temperature, nutrients, light, oxidants and hydrostatic pressure[29,37,48–53]. The ability to synthesize DMSP is highly variable within and between phytoplankton taxa, and intracellular concentrations can range from undetectable levels to as high as 1 M[54,55]. Genes encoding the *S*-methyltransferase enzyme of the transamination pathway for DMSP synthesis, believed to be the major synthetic pathway, have been identified in most dinoflagellates, haptophytes, corals and some diatoms (*DSYB*) and bacteria (*dsyB*)[56,57] (Box 1). The presence of *dsyB* or *DSYB* in an organism is a robust indicator of its ability to produce DMSP, and *dsyB* or *DSYB* transcript and/or their protein abundance can be used to gauge the contribution to environmental DMSP[56,58].

Despite the correlation between the presence of *DSYB* and the host algae producing DMSP to high intracellular levels, there are many instances in which, for example, low DMSP producers contain *DSYB*[56,59]. Conversely, in some algae that generally produce low intracellular DMSP levels (diatoms and potentially the chlorophyte *Pycnococcus provasolii*), the *S*-methyltransferase step is instead catalysed by TpMMT, the product of a different gene[60]. TpMMT has been ratified only in *Thalassiosira pseudonana*[60], and further work is required to establish its validity as a reporter of DMSP synthesis. There are also two other pathways for DMSP synthesis: the methylation pathway in plants[61] and bacteria, for which the methionine *S*-methyltransferase is encoded by *mmtN*[35,62], and the decarboxylation pathway in the dinoflagellate *Crypthecodinium cohnii*[63], with no identified gene.

DMSP conversion to DMS

A large proportion of marine DMS production arises from the bacterial catabolism of dissolved DMSP (DMSPd). DMSP is released from algal and bacterial cells into the dissolved phase following grazing[64,65], viral lysis[66,67], autolysis or senescence of stressed cells[48,68] or active exudation by healthy cells[50,69]. This highly labile DMSPd is imported and catabolized via two dominant microbial degradation pathways: bacterial demethylation (responsible for ~75% of the dissolved DMSP degradation), which potentially generates methanethiol[58], and cleavage (~10% of the DMSPd degradation), which produces DMS[29,30,70,71]. In the Mediterranean Sea, for example, 6–20% of the available DMSP was converted to DMS over an annual cycle[72].

Algal DMSP lysis occurs indirectly during senescence and when cells are grazed by zooplankton or virally lysed, allowing intracellular stores of DMSP to come into contact with intracellular and extracellular lyases[67,73,74]. Microzooplankton grazing can dominate overall phytoplankton mortality, thus exerting an important control on the production of DMS from DMSP in certain environments. In the Mediterranean example, grazing-mediated DMS production explained 73% of the variance in DMS concentrations[72]. Nevertheless, many phototrophic and heterotrophic DMSP producers contain DMSP lyase enzymes and can therefore generate DMS without exogenous sources of dissolved DMSP[75–78], potentially as a carbon and sulfur overflow mechanism to control intracellular DMSP concentrations[50] or liberate DMS and acrylate as signalling molecules, with roles in grazing deterrence[73] or prey detection[79,80] (Box 1). There are eight known DMSP lyase enzymes (DddD[81], DddL[82], DddQ[83], DddW[84], DddY[85], DddK[86], DddP[87] and DddX[88]) found in some bacteria, fungi and viruses, and as yet only one (Alma1 (ref. 75)) identified in algae. Many organisms have DMSP lyase activity but lack these known enzymes, so there are more novel enzymes to discover[89]. As much as 20% of sea surface bacteria contain DMSP lyase enzymes, including important Roseobacters, SAR11 and Oceanispiralles bacteria[56].

There are other, probably minor, pathways for DMS production from, for example, the reduction of the dimethylsulfoxide (DMSO) through a DMSO dimethylsulfoxonium propionate (DMSOP) intermediate. In this pathway, DMSOP is synthesized by algae alongside DMSP, then transferred to the dissolved phase by permeative diffusion or directly via cellular degradation[90,91] and readily metabolized by marine bacteria to produce DMSO[92,93] (Fig. 2). Both various phytoplankton[94] and marine Proteobacteria and Archaea[95] can reduce DMSO to DMS using DMSO reductases. Although DMSO is often detected in marine samples at levels comparable (up to hundreds of nanomolar) to DMSP[92,93,96–98], this is unlikely to be a major DMS source in oxic and photic environments, with evidence that >94% of DMSO in temperate coastal waters is dissimilated to CO_2, with the remainder potentially further oxidized to dimethylsulfone[93]. A further source of DMS is the methylation of methanethiol (MeSH) produced via DMSP demethylation (Fig. 4), which is catalysed by diverse bacteria via an MddA enzyme[99,100].

Pathways competing for DMSP limit DMS production

The major catabolic pathway diverting exogenous DMSP away from DMS generation is the demethylation pathway, thought to account for up to 75% of catabolic breakdown of DMSP[70,101,102] (Fig. 4). In almost all surveyed marine environments, DMSP demethylation potential outweighs that for any individual DMSP lyase pathway, with ≥20% of bacteria in surface waters generally predicted to contain *dmdA* (a marker for DMSP demethylation potential)[103]. In some bacteria, DMSP demethylation is upregulated by the presence of acrylate, the product of DMSP cleavage, potentially diverting further from DMS production[104].

Various DMSP-producing phytoplankton, particularly dinoflagellates, and the bacterium *Pelagibaca bermudensis* (the only bacterium tested) produce other sulfonium compounds from DMSP, including gonyol[105], gonylauline[106], dimethylsulfonioacetate[107] and DMSOP[92]. Many of these DMSP analogues can be catabolized by bacteria to generate DMS or DMSO and/or methanethiol, but in certain cases they can inhibit volatile production[92,108,109]. Thus, microbial modification of DMSP can limit the flux to DMS production by inhibiting DMSP lyase enzymes or by reducing the amount of DMSP available for DMS generation.

Some marine organisms are able to import and accumulate DMSP intracellularly as an osmoprotectant (for example, in *Vibrio* species of marine bacteria[110]) and antioxidant (for example, the marine diatom *Thalassiosira weissflogii*[111]). This import can divert DMSP away from DMS production pathways, highlighting the diversity of roles that DMSP has in marine microbial ecology. Phagotrophic protists, which dominate the microzooplankton and ingest between 40% and 100% of available phytoplankton DMSP per day[72,112], could assimilate up to 30% of DMSP as structural sulfur, with the remainder accumulating in cells as undigested DMSP until release or transformation to DMS via algal prey DMSP lyases[113].

DMS consumption processes

The flux of DMS to the atmosphere is substantially modulated by a combination of biological and photochemical degradation processes in the surface ocean[114], keeping DMS concentrations at low nanomolar levels[23]. DMS is subject to rapid photochemical oxidation in the upper ocean layers[27,115–117], with notable regional and seasonal variability[118]. Loss of DMS via photochemical oxidation is estimated at 17–20 Tg S per year[118].

The remaining DMS produced in the upper layers of the ocean is microbially degraded[119–121], as many microorganisms catabolize DMS to yield electrons for carbon fixation and/or energy (Fig. 4). These include some anoxygenic phototrophic purple sulfur bacteria[122] and phototrophic green sulfur bacteria[123], which use a DMS dehydrogenase enzyme (DdhABC)[124]. Furthermore, some bacteria can use DMS as a source of sulfur, such as *Marinobacter*[125] in a process requiring light, and *Rhodococcus* via a monooxygenase enzyme[126]. Some methanotrophic and ammonia-oxidizing bacteria degrade DMS using methane and ammonia monooxygenase enzymes[127]. Similarly, methylotrophic bacteria such as *Hyphomicrobium*[128] use flavin-dependent DMS monooxygenase (DmoAB)[129] to generate methanethiol and formaldehyde from DMS (Fig. 4). DMS monooxygenase is present in 0.5–3.4% of bacteria in seawater and marine sediment samples[130]. Microbial methanethiol oxidases (MtoX) further degrade methanethiol to formaldehyde as a carbon or energy source[131–133]. Some Gammaproteobacterial *Methylophaga* spp. are known to contain MtoX[132] and are important DMS consumers in coastal waters[134], but their key enzyme demethylating DMS is unknown.

Analysis of DMS-related gene abundance and expression profiles in omics data sets, such as those collected as part of the *Tara Oceans* expeditions[135], can infer potential environmental DMSP and DMS production, imply the key protagonists and predict DMS hotspots[59,136,137]. As heterotrophs can make DMSP, environments with high DMSP production do not need to be oxic and/or photic, and novel hotspots for DMSP and DMS production might be uncovered as molecular tools become

DMS emission by macroalgae discovered[226]

DMSP demonstrated to be DMS[227]

DMS emissions restricted to salt and brackish water species[228]

DMS key in transfer of sulfur from sea to land[225]

Sulfur cycle involved in bio-controlled thermostasis?[4]

First data on DMSO distribution in marine waters[229]

Henry's law constants for DMS in freshwater and seawater determined[231]

First estimate of DMS sea–air flux[230]

Grazing by zooplankton on phytoplankton is the key mechanism of DMS release to seawater[232]

Evidence for biological removal of DMS from seawater[234]

CLAW hypothesis: bio-regulation of climate via effect of temperature and sunlight on DMS production[1]

Confirmation of role of bacteria in DMSP conversion to DMS[235]

Estimation of global ocean-to-atmosphere DMS flux[233]

Correlation among seasonal DMS, MSA and SO_4 in marine air observed[168]

Two-year seasonal record of atmospheric and oceanic DMS in remote Southern Hemisphere[156]

Ice diatoms revealed as new and significant DMS source[239]

Insights into biological cycling of DMS and DMSP in oceanic samples[237]

Evidence that DMS used as foraging cue by Procellariiform seabirds[241]

In situ Lagrangian study constraining surface ocean sulfur budget[238]

Evidence of role of DMSP and DMS in grazing-activated chemical defence in algae[73]

DMSP content of reef corals reported[240]

First global DMS climatology[140]

Evidence of production and release of DMSO by phytoplankton[119]

Evidence that DMSP, DMS and DMSO may serve as a cellular antioxidant system[48]

Evidence of link between specific taxonomic groups of bacteria (*Roseobacter*) and metabolism of DMSPd to DMS in natural communities[242]

Model estimate of response of DMS production and flux to climate change[210]

In situ Lagrangian process study of DMS biogeochemistry within a growing coccolithophore bloom[243]

Comprehensive model study of atmospheric multiphase DMS oxidation[166]

Eddy correlation measurement of DMS sea–air fluxes[143]

Novel gene *dddD* shown to be required for bacterial conversion of DMSP to DMS[265]

Model estimate of climate sensitivity to DMS emissions[244]

Experimental evidence of DMS sensitivity to ocean acidification[245]

Experimental evidence of DMS sensitivity to ocean acidification in the Arctic[246]

Evidence of large contribution of natural aerosols to uncertainty in indirect forcing[17]

Updated global DMS climatology[23]

Evidence of DMS control on Arctic aerosol and cloud processes[248]

DMS control over CCN brought into question[11]

Evidence that corals possess enzymatic machinery necessary for DMSP production[39]

Experimental evidence of DMS sensitivity to ocean acidification in the arctic[247]

Evidence that DMS facilitates tritrophic mutualism within Southern Ocean food web[249]

Model estimate of positive climate feedback as a result of ocean acidification-driven reduction in DMS flux[216]

Evidence of bacterial DMS to DMSO oxidation in the presence of methyl amines using Tmm enzyme[251]

Evidence that marine plastic debris emits DMS signal, which increases its palatability to seabirds[250]

DSYB enzyme that controls DMSP synthesis identified in many phytoplankton and corals[56]

Fully coupled model estimate of climate sensitivity to ocean acidification-driven reduction in DMS flux[217]

Direct evidence of *dsyb*–DMSP production by many sediment-dwelling bacteria[35]

New measurements of atmospheric aerosols show importance of algae-derived DMS for CCN in the North Atlantic[14]

Discovery of major DMS gas-phase oxidation product HPMTF, which could account for >30% of oceanic DMS emissions and strongly influence new particle formation and growth[179]

Identification of new and more rapid DMS atmospheric oxidation pathway[178]

Fig. 1 | History of dimethylsulfide biogeochemistry research. Current understanding of global dimethylsulfide (DMS) biogeochemistry can be attributed to nearly 100 years of research, represented by key publications colour coded by research focus. Early research highlighted the ubiquitous occurrence of DMS in marine waters, eventually leading to the seminal paper by Lovelock et al. in 1972 (ref. 225), which concluded that DMS was the missing link in the global biogeochemical sulfur cycle acting as the main vector of sulfur from the ocean through the atmosphere to the land. By the 1980s, the role of DMS as a climate-cooling gas was becoming clear, culminating in the thesis of Charlson et al. in 1987 (ref. 1) – the CLAW hypothesis. This early research inspired a colourful field of research into the climate role of marine DMS emissions that continues to be pursued to this day. CCN, cloud condensation nuclei; DMSO, dimethylsulfoxide; DMSP, dimethylsulfoniopropionate; DMSPd, dissolved DMSP; HPMTF, hydroperoxyl methylthioformate; MSA, methanesulfonate[1,4,11,14,17,23,35,39,48,56,73,81,87,119,140,143,156,166,178,179,210,216,217,225–251].

more widely used[130,138]. However, there are still many organisms that produce DMSP but lack known DMSP synthesis genes and/or pathways[35]. Thus, current analyses of omics data probably underestimate the potential for DMSP synthesis and subsequent DMS production[137,139]. Moreover, without complementary biogeochemical work such as DMS production and consumption rates, inferences from omics are limited. Robust community segregation techniques (for example, based on size and pigmentation) and measurements of key DMS biogeochemical rates with such molecular work are necessary to better inform on the environmental and biological drivers of the variability in net DMS production rates.

Sea-to-air fluxes and atmospheric fates

The influence of aerosols on the climate of the Earth remains one of the largest uncertainties in global climate models, limiting our ability to quantify their role in the past climate of the Earth and to accurately forecast the climate into the future[17]. The ocean–atmosphere flux of DMS and its rapid atmospheric oxidation contribute to the formation and growth of aerosols and particles (Fig. 5), which have the second greatest influence on natural aerosol indirect forcing after volcanic sources[17]. However, the estimated climate-cooling effect of DMS is associated with a high degree of uncertainty, and improving the accuracy of the ocean–atmosphere flux will be a major step towards constraining its role in climate processes[2,3]. The following section describes global seawater DMS climatologies that have improved DMS flux estimates, atmospheric DMS oxidation processes and the resultant impacts on global radiative forcing.

Sea-to-air fluxes

Accurate calculation of global DMS sea-to-air fluxes requires a reliable representation of surface ocean DMS concentrations. Using a bottom-up approach, global DMS climatologies have been generated from the near-surface observations collated in the Global Surface Seawater DMS database (GSSD; https://saga.pmel.noaa.gov/dms/). These observations are smoothed and interpolated to produce a gridded seawater DMS climatology[23,140]. DMS flux can then be calculated using Flux = $K\Delta C$, where ΔC is the concentration difference between the ocean and atmosphere (atmospheric DMS levels are typically two orders of magnitude lower than in seawater, so ocean concentrations determine the flux magnitude).

K is the gas transfer velocity (cm h^{-1}), primarily a function of wind speed, but implicitly representing the complex physical processes involved in air–sea gas transfer, including diffusion, surface renewal, bubble-mediated transfer and turbulence (wind stress, waves and currents)[141]. Multiple approaches are used to investigate the processes that control K_{DMS} (and for other trace gases), including deliberate dual-tracer release techniques that estimate gas transfer by measuring the evasion of sparingly soluble gases with different diffusivities (^{3}He/SF$_6$)[142] and direct, shipboard measurements of waterside gas transfer using eddy covariance methods[143–145]. Yet, there remains some lack of agreement between parameterizations of K and eddy covariance measurements and somewhat limited understanding of the importance of the processes controlling K under various atmospheric and oceanic conditions[141,146,147]. There are a number of commonly used parameterizations[142,148,149], the choice of which when applied to models can have important impacts on calculated marine DMS emissions[23,146,150]

When the first global DMS climatology was produced in 1999 by Kettle et al.[140] (hence called the K99 climatology), the DMS database contained ~15,000 data points. The next iteration in 2011 (L11)[23] used an updated DMS database, increasing to ~47,000 data points and including changes to the computational algorithm, resulting in a 17% increase in the estimate of global DMS emissions. To date, most atmospheric investigations used the L11 climatology[23] as a primary reference product for global seawater DMS, which predicts a global DMS flux of ~28 Tg S per year when using the parameterization of gas transfer velocity of Nightingale et al.[142]. This flux estimate suggests that emission to the atmosphere turns over the seawater DMS pool (~1 Tg S) every ~13 days. In 2022, the climatology (H22) was updated[151], with the inclusion of >870,000 data points, a reduction in biases related to different observational frequencies, the incorporation of seasonal dynamics and a refined interpolation algorithm. Resultingly, H22 provides more realistic monthly DMS estimates and regional variability than the previous iterations.

Empirical DMS climatologies have also been developed using relationships with phytoplankton chlorophyll and parameters that describe light penetration into the surface ocean[24,152,153]. Furthermore, machine learning has been used to develop climatological DMS fields, with the aim of capturing nonlinear relationships between environmental variables and DMS concentrations[25,154]. An advantage of the empirical and neural network approaches is that they capture regionally specific interannual variability in the magnitude and timing of seasonal variations in seawater DMS. Over a 14-year period of satellite observations in the North Atlantic, for instance, estimated DMS concentrations during the productive season appear to vary threefold and the annual peak in DMS concentrations ranged over 2–3 months[24].

Atmospheric fate of DMS emissions

The atmospheric DMS burden is estimated at 9.6–140 Gg S[18,19,155], most of which exists in the lower troposphere below ~2 km. Combining the atmospheric burden with the sea-to-air emission flux implies a global mean lifetime of DMS in the atmosphere of 1.2–2.1 days[18–20]. The atmospheric mixing ratio of DMS in marine environments is typically a few hundred parts per trillion (ppt)[20]. Atmospheric DMS levels and lifetime also vary owing to complex physical and chemical interactions over different timescale and space scale. Large-scale meteorological factors (such as atmospheric boundary layer height, stability and variations in wind speed) influence sea-to-air flux strength and marine boundary

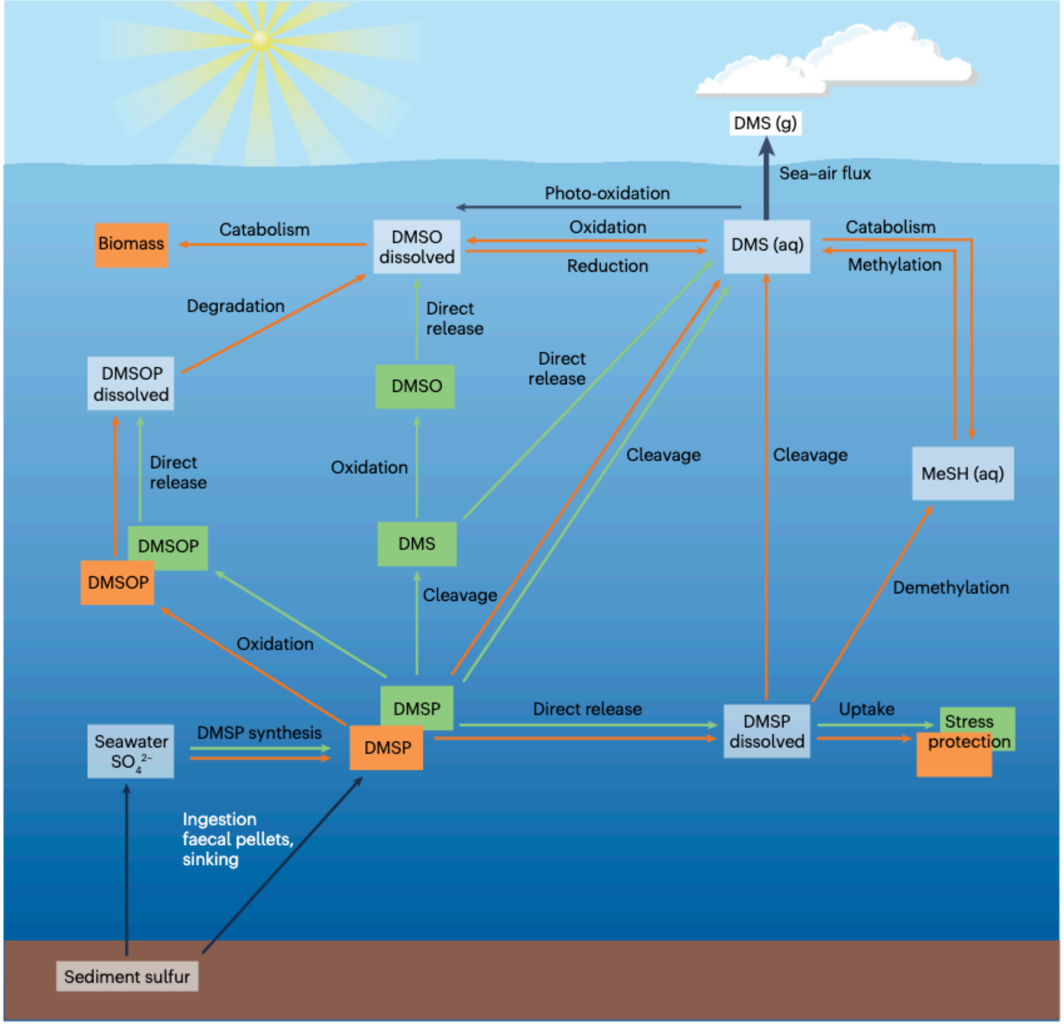

Fig. 2 | The marine biogeochemical dimethylsulfoniopropionate and dimethylsulfide cycle. Dimethylsulfoniopropionate (DMSP) is produced by algae (through pathways marked by green boxes and arrows) and bacteria (orange boxes and arrows), with seawater sulfate (SO_4^{2-}) serving as the sulfur source for DMSP synthesis. Some algal and bacterial DMSP producers release DMSP and/or derived metabolites (dimethylsulfoxonium propionate (DMSOP), dimethylsulfoxide (DMSO) and dimethylsulfide (DMS)) into seawater. Dissolved DMSP or DMSOP can be imported for stress protection or catabolism by bacteria to produce other sulfur compounds (DMS, methanethiol (MeSH) and DMSO), which can also be consumed by bacteria. The majority of dissolved DMSP is used as an energy, carbon and/or sulfur source by the bacterial demethylation pathway, potentially generating MeSH and not DMS. By comparison, much less dissolved DMSP is enzymatically cleaved by bacterial and algal DMSP lyases to produce DMS than via the demethylation pathway. Any DMS that survives bacterial consumption and/or oxidation and photo-oxidation (<10% of the total production) drives the ocean–atmosphere concentration difference and sea-to-air flux. Dissolved and aqueous components indicated through blue boxes.

layer (MBL) concentrations, and photochemical cycles produce diel variations in primary oxidants[156–158]. DMS can also dissolve in cloud droplets or aerosols, where rapid reactions lead primarily to the production of DMSO, methanesulfonate (MSA) and non-seasalt sulfate (n.s.s.-SO_4^{-})[159,160]. Aqueous-phase reactions with ozone contribute up to 78% to the in-cloud DMS sink, although this is <10% of the total MBL DMS sink[161–163].

The oxidation of DMS is key to its fate in the marine atmosphere and its role in new particle formation and cloud-related processes (Fig. 5), and the balance between different multiphase reactions determines the influence of DMS[163,164]. There are two interconnected pathways for DMS oxidation (abstraction and addition), determined in large part by the nature of the oxidants involved[165] (Fig. 5). In broad terms, atmospheric DMS reacts with hydroxyl radicals (•OH) during the day and with nitrate radicals (•NO_3) at night. In reality, the oxidation reaction chemistry involves complex and multiple gas-phase and particle-phase intermediates[165]. For example, BrO and IO have key roles in atmospheric sulfur chemistry by enhancing DMS oxidation rates and reducing the SO_2 yield[166,167]. Modelled estimates approximate a 3:1 addition:abstraction ratio, but the relative proportions depend on which oxidation reactions are included and whether gas-only or multiphase processes are considered[20,163,165].

Next Page

The products of the abstraction and addition pathways (n.s.s.-SO_4^- and MSA) are closely associated with small, recently formed particles[14,168]. The abstraction pathway can promote new particle formation and ultimately generate SO_2 and H_2SO_4. The addition pathway typically leads to the generation of DMSO and contributes to the growth of existing particles. Gas-phase reaction of MSIA with OH generates SO_2 and subsequently H_2SO_4, thus promoting new particle formation[169,170]. There is increasing evidence of the important role that MSA has in new particle formation[171–174], which might involve bimolecular interactions between MSA and H_2SO_4. There is also some evidence that new particle formation is enhanced when MSA or MSIA combines with water vapour, amines or ammonia to form molecular clusters[175–177].

An additional branch of the abstraction pathway was described in 2019 that leads to a previously unidentified DMS oxidation product, hydroperoxyl methylthioformate (HPMTF[178,179]), altering current understanding of DMS oxidation of the MBL (Fig. 5). Up to ~50 ppt HPMTF was observed in the lower 2 km of the marine atmosphere[179], and initial findings suggest that approximately one third of atmospheric DMS could be converted to HPMTF via an isomerization pathway.

Nevertheless, an explicit description of the exact mechanism by which DMS oxidation products contribute to new particle and CCN formation and/or growth has proved elusive. There are multiple DMS oxidation products and pathways that occur in various phases (gas, aerosol and cloud), which are influenced by the ambient atmospheric conditions (including oxidants, humidity and particle surface area). New particle formation in the MBL is uncommon[180], but the conditions do encourage the growth of existing particles. Conditions in the free troposphere are much more conducive to new particle formation but tend to limit particle growth.

Observational and modelling advances on particle formation and CCN processes in the MBL have revealed strong evidence of a link between DMS emissions from ocean biology and aerosol or cloud properties. Primarily focused on the Southern Ocean, this evidence demonstrates that synoptic-scale uplift events mix DMS-rich air up out of the MBL into the free troposphere where conditions favour particle formation[13]. They highlight the importance of sea ice regions as a source of biogenic CCN in the summer months, wherein high DMS flux, low sea-spray surface area and cold temperatures can stimulate new particle formation and growth, sometimes even within the MBL[181]. Furthermore, the long-range transport of DMS-rich air parcels, combined with precipitation scavenging and cloud processing (which leads to the substantial growth of biogenically formed particles), explains the observed variability in Southern Ocean MBL CCN concentrations[13,15,182].

In the past, global climate models have often ignored key DMS oxidation intermediates to minimize computational costs[166,183–185]. Progress to increase the complexity of the atmospheric sulfate chemistry schemes includes the inclusion of DMS oxidation by halogens[186], the impact of MSA on size distributions[174] and the inclusion of OH-addition, H-abstraction and the associated isomerisation pathway[18]. As a result, there is improved agreement between modelled and observed concentrations of DMS and other key components of the atmospheric sulfur cycle[18].

Uncertainties in DMS flux estimates and climate effects

There is currently weak evidence for a biologically controlled DMS–climate feedback (CLAW) on both regional and global scales[9,10,187,188]. Field observations from key DMS emission regions do, however, demonstrate a direct link between DMS from phytoplankton blooms and cloud radiative properties[12–15], implying that DMS is important for longer term climate. The ability of models to accurately estimate the present-day ocean flux of DMS and its subsequent climate effects is still greatly limited by a number of crucial uncertainties, resulting in a lack of agreement between models (reviewed elsewhere[150]) and between models and observations (reviewed elsewhere[189]). The ability of models to predict seawater DMS and estimate current and future DMS fluxes and climatic impacts remains poor[150,190].

Estimates of the contribution of DMS emissions to radiative forcing combine climatological seawater DMS concentration estimates with aerosol–chemistry–climate general circulation models to derive a top of the atmosphere global cooling effect of −1.7 to −2.3 W m^{-2}

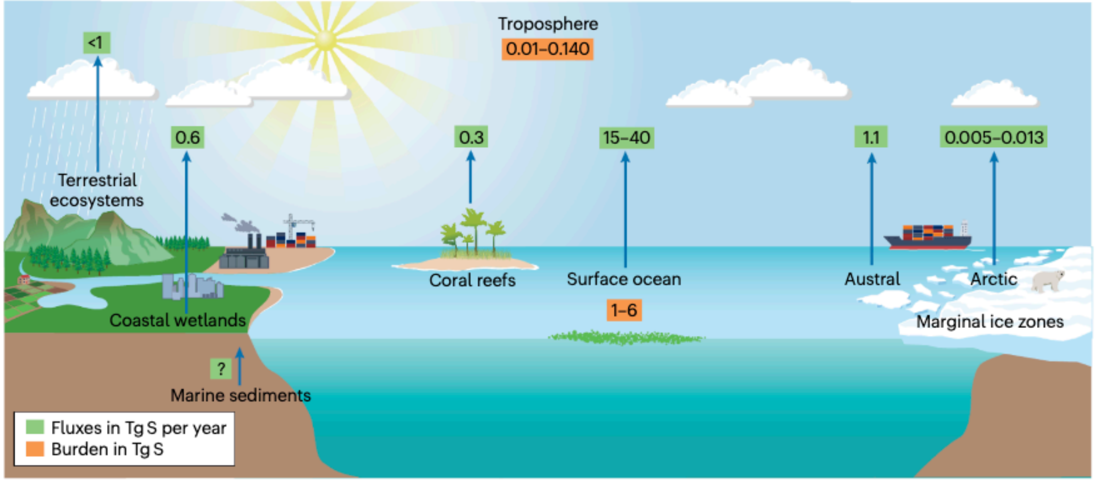

Fig. 3 | DMS fluxes and burdens. Fluxes from global marine and terrestrial environments (Tg S per year, green) and dimethylsulfide (DMS) burden for surface ocean and troposphere (Tg S, orange). Most DMS emissions are from the ocean. Tropical coral reefs are also hotspots for atmospheric DMS flux[252], as dimethylsulfoniopropionate biosynthesis is upregulated by stressors, resulting in extreme spikes in atmospheric DMS concentration observed above reefs during stress events[253]. Estimates are included for the troposphere[18,19,155], terrestrial ecosystems[254], coastal wetlands[255], marine sediments[35,37], coral reefs[47], the surface ocean[23,25,256], austral marginal ice zones[257] and Arctic marginal ice zones[258].

Box 1

Biochemistry of dimethylsulfoniopropionate production

Three dimethylsulfoniopropionate (DMSP) synthesis pathways have been identified: transamination[259], methylation[46,50,260] and decarboxylation[63,261].

Transamination

The committed step of this pathway is catalysed by a methylthiohydroxybutyrate *S*-methyltransferase enzyme[259], encoded by the bacterial *dsyB* gene that occurs in up to 0.6% of the surface seawater bacteria. This pathway is proposed to have originated in bacteria, and functional DsyB-like enzymes (with ~30% amino acid similarity to DsyB), termed DSYB, exist in most dinoflagellates, haptophytes and corals and ~20% of diatoms[56].

Methylation

DMSP production in plants occurs through two distinct methylation reactions. Methionine (Met) is first *S*-methylated via the *S*-methyltransferase enzyme, MMT, to generate *S*-methyl methionine (SMM)[61,262]. The plant MMT enzyme, which is involved in an SMM cycle that modulates free methionine and *S*-adenosyl methionine levels[263], has not formally been shown to be involved in DMSP production in any plant, and none of the downstream plant DMSP synthesis genes has been identified for either pathway.

Various Alphaproteobacteria, Gammaproteobacteria and Gram-positive Actinobacteria also produce DMSP via a methylation pathway[35,62]. The bacterial methionine *S*-methyltransferase, MmtN, shares only 30% amino acid identity to the N-terminal domain of the plant MMT and is approximately three times smaller[35]. The bacterial *mmtN* gene is often adjacent to genes encoding enzymes that function downstream of SMM in DMSP production via their methylation pathways[35,62]. Much like *DSYB/dsyB*, the presence of *mmtN* is a robust indicator of DMSP production, but bacteria with this gene are very rare (~0.03% of bacteria) in seawater[35]. Additionally, a methionine *S*-methyltransferase isoform enzyme (BurB) exists in Betaproteobacterial *Burkholderia* spp. that produce DMSP as an intermediate in the production of a cyclopropanol virulence factor[264], but this system is extremely rare in marine metagenomes.

Decarboxylation

The dinoflagellate *Crypthecodinium cohnii* is proposed to make DMSP via a decarboxylation pathway. Met is first decarboxylated to produce methylthiopropanamine, which is deaminated and oxidized to form methylpropionate. Then, methylpropionate is methylated to form DMSP[63]. A methionine decarboxylase enzyme has been characterized but not identified. However, *C. cohnii* also contains five DSYB homologues[56], thus its method of DMSP synthesis needs to be revisited.

(refs. 2,3,18,21). Radiative effect estimates are highly sensitive to the sea-to-air DMS flux and are thus determined by variations in surface ocean DMS and the choice of DMS gas transfer velocity parameterization. There is still considerable uncertainty with and between different flux estimates (anywhere between 9 and 40 Tg S per year)[191,192], and the knock-on effect is an associated uncertainty in radiative forcing of ± 0.7 W m^{-2} (refs. 2,193). Global DMS climatologies derived from the GSSD are used in many climate models to provide a representation of surface ocean DMS concentrations that can be used to estimate sea-to-air fluxes. Though continually growing in complexity[151], the available climatologies are still limited by relatively sparse observations in space and time, resulting in only limited understanding of global and regional DMS distribution. Although cloud processes in some regions can thus show large responses to DMS perturbations in models, DMS observations can be completely absent in these key regions[3]. At global scales, a switch from the K99 to the L11 climatology adds a further −0.3 W m^{-2} to the overall DMS-derived cooling, a result of a much larger database of observations that leads to greater production of H_2SO_4 and associated particle formation[2].

L11 (ref. 23) assessed the flux uncertainty inherent in the choice of gas transfer velocity parameterization (−37% to +15%) and the uncertainty associated with variability in seawater DMS observations (−14 to +44%). The uncertainties are comparable, which highlights the need to better constrain the DMS gas transfer velocity and the primary mechanisms that control seawater DMS variability. For example, direct observations of DMS gas transfer velocity suggest that the relationship with wind speed is not as strong as suggested by many parameterizations[142,148,149] used in quantifying global climatological DMS fluxes. The weaker relationship between wind speed and DMS gas transfer velocity[146] is likely to be because DMS is relatively soluble (compared with CO_2) and its gas transfer velocity is much less sensitive to the bubbled-mediated component of the flux[141].

Further uncertainty is introduced depending on whether a bottom-up (observation-based climatology) or top-down (empirically derived climatology) approach is used to generate climatological seawater DMS fields. For example, different estimates of the regional North Atlantic flux in May vary between 1.6 and 2.9 Gg S per day (ref. 189). Global DMS derived from satellite observations combined with an empirical relationship[24] and an artificial neural network approach[25] both suggest lower DMS fluxes (~18–20 Tg S per year) than L11 using the same gas transfer velocity parameterization[25]. By contrast, the H22 DMS climatology takes advantage of a substantial (~18-fold) increase in DMS data[151]. Using the same wind field and gas transfer velocity parameterization, H22 reveals large regional variations compared with L11, but the global DMS flux is <5% different. More work is needed to identify the relative merits and/or inaccuracies of the different approaches for estimating surface seawater DMS concentration[189].

To predict DMS flux, Earth System Models (ESMs) use either empirical parameterizations to compute DMS from chlorophyll and other key oceanographic variables (for example, mixed layer depth, MLD) or prognostic models that include representations of marine biota and simple parameterizations of key processes that control

DMS release (for example, grazing, cellular exudation and cellular lysis)[150]. Uncertainty is introduced by the simplistic representation of marine ecosystem structure within global prognostic DMS models, limiting their capability to constrain DMS production and flux in the present day and their ability to predict DMS into the future. Increased complexity has been integrated into biogeochemical models within some ESMs, with up to five explicit functional groups of phytoplankton (2 × Phaeocystis, diatoms, diazotrophs and smaller phytoplankton) and two implicit groups (coccolithophore and cyanobacteria), as well as improved representation of marine sulfur cycling[187]. However, existing global DMS prognostic models do not account for the specific contributions from different phytoplankton species to the overall net production of DMSP and DMS[189] and completely neglect the important bacterially driven processes that predominantly drive DMS production[30]. The ability of models to simulate observations are therefore limited[189] and have large uncertainties in predicting future DMS flux.

The current challenge is illustrated when predicting trends in surface ocean DMS concentrations and fluxes using four current-generation ESMs[150] (Fig. 6). The modelled changes in DMS concentrations are predominantly correlated with marine productivity, but the

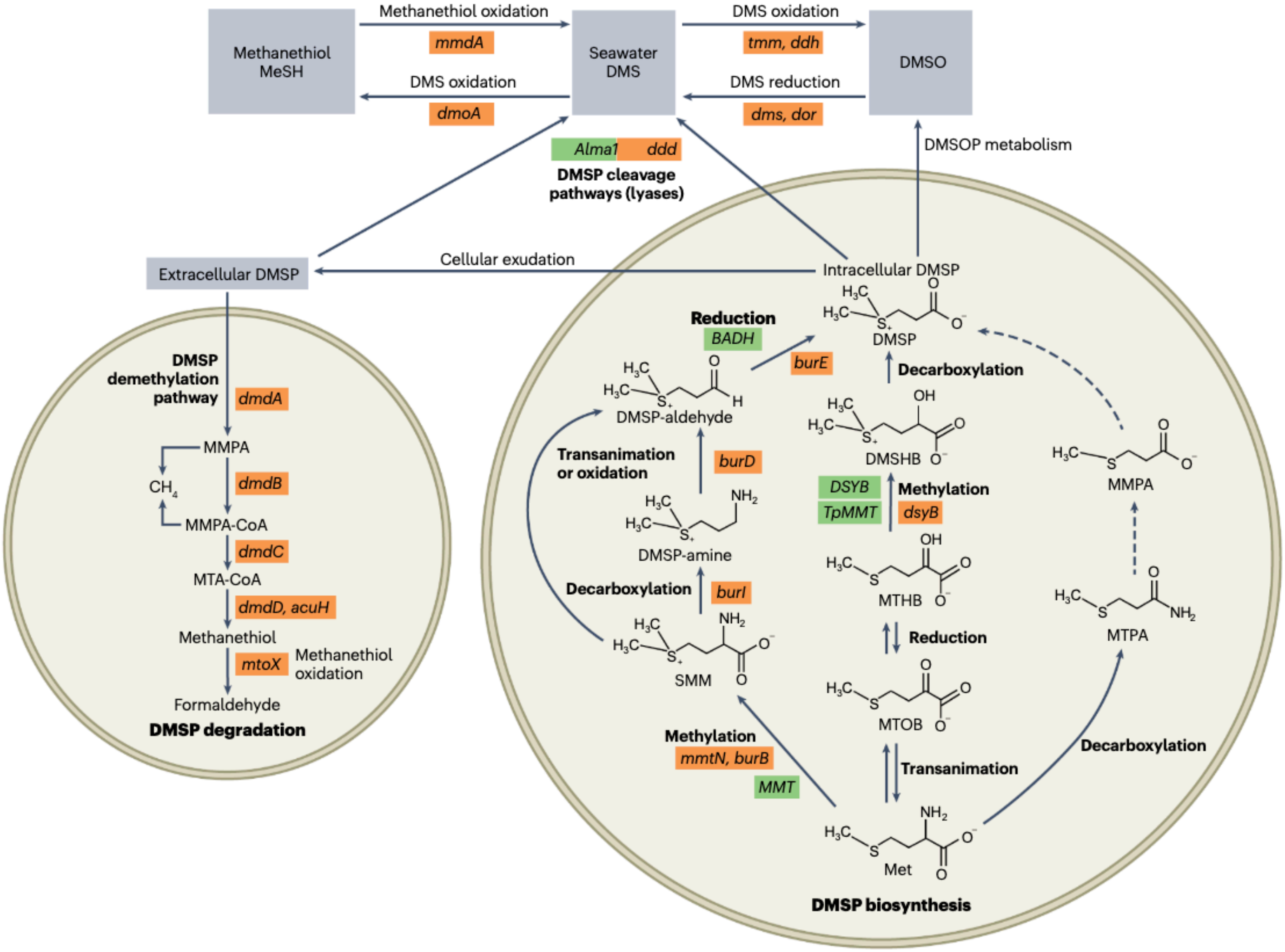

Fig. 4 | Dimethylsulfoniopropionate biosynthesis and degradation. Where known, the genes encoding key enzymatic steps are indicated in italics: orange for bacterial or green for algal. Grey boxes indicate dimethylsulfide (DMS), dimethylsulfoniopropionate (DMSP) DMS and methanethiol (MeSH) dissolved in seawater, and circles encompass intracellular processes. Dashed lines represent proposed pathways that require ratification. Three pathways for DMSP biosynthesis that lead to the formation of intracellular DMSP have been identified (circle on right): the transamination pathway, the methylation pathway and the decarboxylation pathway. The transamination pathway dominates in marine systems (key enzymes *DSYB*, *TpMMT* in algae, *dsyB* in bacteria), and the methylation pathway is mainly seen in plants (*MMT*) and some bacteria (*mmtN*). The decarboxylation pathway requires further ratification. DMSP can be degraded via DMSP cleavage pathways to produce DMS (*ddd* in bacteria and *Alma1* in algae) and via demethylation (*dmdA*, *dmdB*, *dmdC*, *dmdD*, *acuH* and *mtoX*), resulting in the formation of MeSH and formaldehyde (left circle). Seawater DMS is oxidized to dimethylsulfoxide (DMSO) (*tmm* and *ddh*), which can then be reduced back to DMS (*dms* and *dor*), or to MeSH (*dmoA*), which can also be oxidized back to DMS (*mmdA*). DMSHB, methylthiohydroxybutyrate; DMSOP, dimethylsulfoxonium propionate; MMPA, methyl-3-mercaptopropionate; MMPA-CoA, methyl-3-mercaptopropionate coenzyme A; MTA-CoA, 3-methylthioacryloyl coenzyme A; MTHB, methylthiohydroxybutyrate; MTOB, methylthiooxobutyrate; MTPA, methylthiopropanamine; SMM, *S*-methyl methionine.

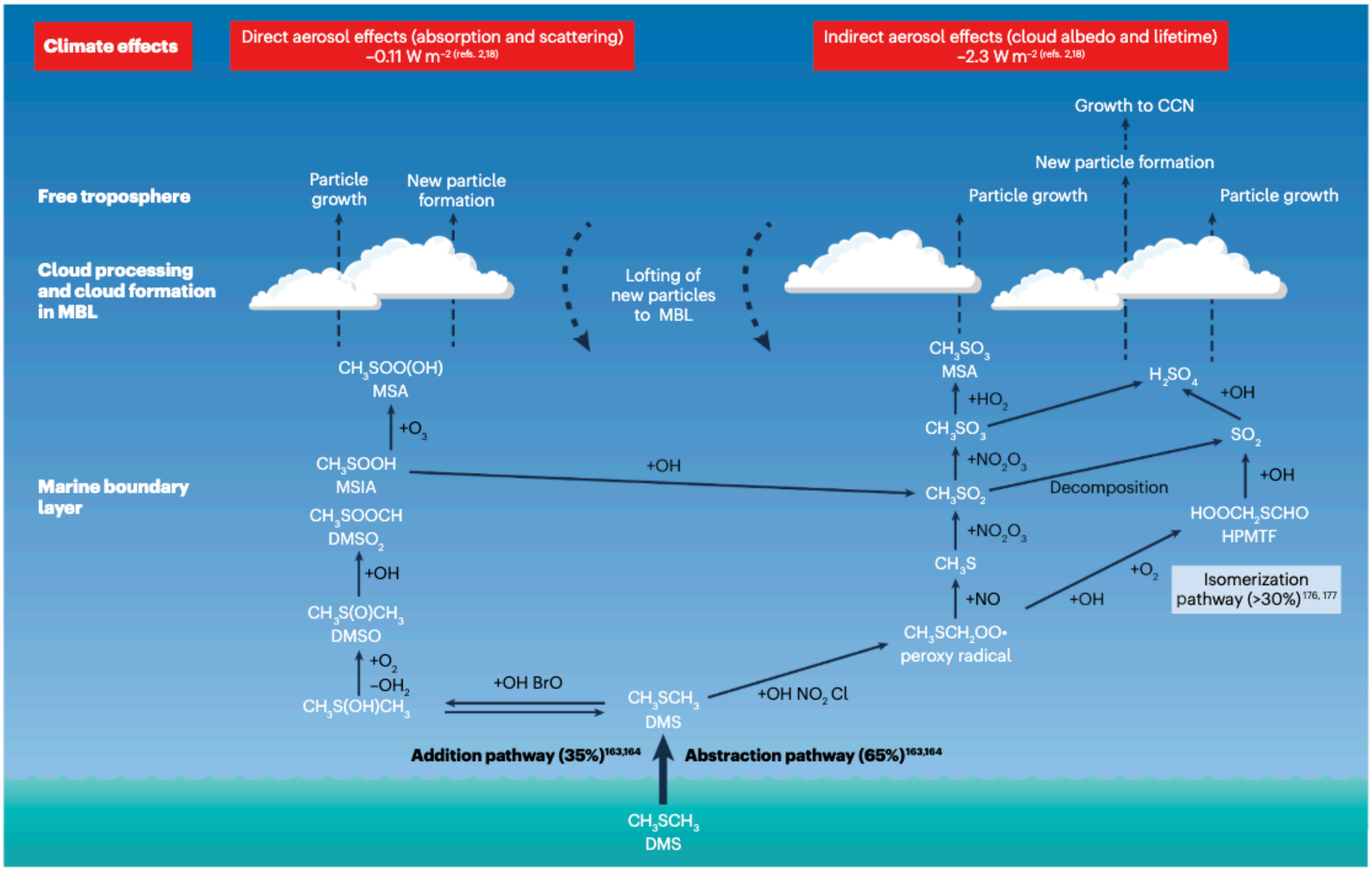

Fig. 5 | Atmospheric dimethylsulfide-related processes. The atmospheric oxidation pathways of dimethylsulfide (DMS) and effects on particle formation and growth, and cloud radiative properties. The abstraction pathway promotes new particle formation and generates SO_2 and H_2SO_4, whereas the addition pathway contributes to the growth of existing particles and the formation of dimethylsulfoxide (DMSO) and methanesulfonate (MSA)[165,166]. The isomerization pathway (first described in 2019)[178,179] could account for around one third of DMS oxidation to form hydroperoxyl methylthioformate (HPMTF), altering current understanding of marine boundary layer (MBL) DMS oxidation. Climate effects arise from both direct and indirect aerosol effects[2,18]. CCN, cloud condensation nuclei; MSIA, methanesulfinic acid.

model simulations provide no consensus in long-term trends (Fig. 6). This lack of consensus is driven by an absence of realistic representation of biological processes in existing empirical parameterizations and large uncertainty in the future evolution of marine primary production and variations in species composition. Future work requires models and parameterizations to better represent process understanding, by increasing the complexity of lower trophic ecosystem dynamics in DMS parameterizations and models.

Summary and future perspectives

The evidence for biological climate control through DMS is still unclear, but marine DMS clearly has a profound influence on atmospheric and climate-related processes[2,3,22]. DMS emissions influence biogenic particle formation, which impacts new particle formation and cloud albedo[12–16], affecting global radiative forcing[2,3,18,21]. However, there are fundamental uncertainties about the spatial and temporal variations in surface ocean DMS concentrations and the modelling of sea-to-air fluxes. These uncertainties prevent accurate simulation of DMS in ESMs and hinder the prediction of DMS influence on future climate of the Earth.

In this final section, we explore areas that require future research efforts, including the potential for molecular genetics tools to further our understanding of the biological drivers of DMS production. We also recommend ways to explore the influence of a changing climate on DMS biogeochemistry and to improve predictions by ESMs.

Advancing molecular understanding and modelling capability

Genetics and molecular biology-based techniques have revealed that an array of microorganisms across marine environments are capable of influencing global DMS production from equally diverse marine environments. However, there are limitations and challenges in using these methods. Molecular genetics only report the potential for DMS and DMSP cycling. Analysis of global omics data sets such as Tara Oceans[135], although informative, is not backed up by DMSP and/or DMS process measurements, and smaller-scale molecular research generally lacks measurements of DMSP and DMS synthesis and turnover rates. Future research must link knowledge of the functional enzymes and pathways, molecular microbial ecology and robust DMSP and DMS production and cycling measurements[194,195].

In particular, the processes that drive net DMS production in the surface ocean – the net outcome of the associations and interactions within the microbial community – are difficult to model and predict, particularly in highly productive bloom environments[189]. To address this bottleneck, trait-based community model approaches[196] should combine with omics to define specific microbial communities. This approach could provide information on how shifts in trait values under different environmental conditions impact the production of DMSP and DMS by influencing the gene expression of key enzymatic pathways. It would also improve the ability of mechanistic models to predict the influence of climate change-driven microbial community composition shifts on net DMS production. Investigation of variations in synthesis, accumulation and metabolism of DMSP between organisms with nutritional strategies could provide a basis for modelling DMS production that contrasts with the approach of assigning DMSP cell quotas to different phytoplankton groups[197–199].

Given the key role DMS plays in climate regulation, it is vital to have an accurate understanding of global DMS surface ocean concentrations and fluxes, to improve model estimates of the influence of DMS on climate now and into the future. However, there is a large disconnect between the current level of biogeochemical and molecular understanding and present-day modelling capability. ESMs currently rely on DMS parameterizations that use physical parameters plus poorly constrained relationships with phytoplankton biomass to estimate global DMS concentrations and fluxes[150]. Increasing the accuracy of models requires improved representation of the controls on DMS production, which can only be achieved through multidisciplinary, co-designed research. Since the mid-2000s, advances in analytical techniques led to automated DMS measurement systems capable of high-resolution spatial and temporal data coverage[144,200–203]. Future investment should focus on the technological development of low-cost, low-energy DMS sensors that can be deployed autonomously, for example, on Argo floats or unmanned vehicles[204–206] to collect data from under-sampled regions or during transient events such as dust-stimulated blooms[207]. The ability to collect data in this way, combined with existing ship-deployed automated systems, would present further opportunities to explore regional and global patterns in oceanic DMS distributions[25,208]. To develop accurate, global-scale models of surface ocean DMS, future work should use machine-learning methods to interrogate high spatial and temporal frequency oceanographic data sets (with data including standing stocks of DMS and DMSP, process rates of DMSP synthesis, DMSP turnover, biological DMS consumption/production and high-frequency microbial community composition).

Impact of acidification

The impacts of ocean acidification on DMS production primarily are investigated with in situ mesocosm experiments that target whole surface ocean communities from various geographical locations, often under highly productive bloom conditions[209]. DMS concentrations tend to decline under future ocean acidification conditions (in seven out of nine published mesocosm experiments), suggesting that net DMS production is influenced by ocean acidification. However, unravelling the complex processes that could be driving this response is challenging and could include changes to plankton community structure, grazing rates on phytoplankton, the activity of DMSP lyase enzymes and bacterial metabolism of DMSP to DMS. As modelling projects the DMS flux into the future under different climate change scenarios[210–215] by applying and upscaling the results of these mesocosm experiments[216,217], longer scale and more sophisticated experiments are needed.

Ocean acidification is not occurring in isolation, so a future priority should be the manipulation of multiple forcing factors, such as ocean acidification, deoxygenation, nutrient availability, temperature and light over evolutionary timescales (tens to hundreds of generations)[218]. The use of single-species algal cultures is needed to understand the physiology of individual species in multispecies models, with the caveat that important ecological and biogeochemical interactions are excluded. Previous mesocosm experiments have been limited to predominantly coastal environments and experimental durations of <4 weeks and often considered the response of DMS to ocean acidification as a single stressor. Although technically and logistically challenging, longer-term multistressor ecological-level experiments are required to fill key knowledge gaps. These experiments should be paired with omics analysis and in situ rate measurements of key processes (such as size-fractionated DMSP and DMS consumption and production) to determine the processes most sensitive to future change. Information from such experiments would provide an indication of physiological plasticity and could be used to improve the mechanistic representation of DMS-related processes in ESMs[209].

Potential impact of climate mitigation strategies

Focused geoengineering measures including carbon capture and storage, artificial upwelling of nutrients, alkalinity enhancement, albedo enhancement and iron fertilization[219] have been proposed to help mitigate the climate crisis. Any geoengineering activity has potential consequences for the marine sulfur cycle, but these responses are poorly quantified. The DMS response is comparatively most understood in oceanic iron fertilization and has responded in various ways: increased DMS production was observed in the Equatorial Pacific and Southern Ocean experiments, whereas little change or a decline was observed

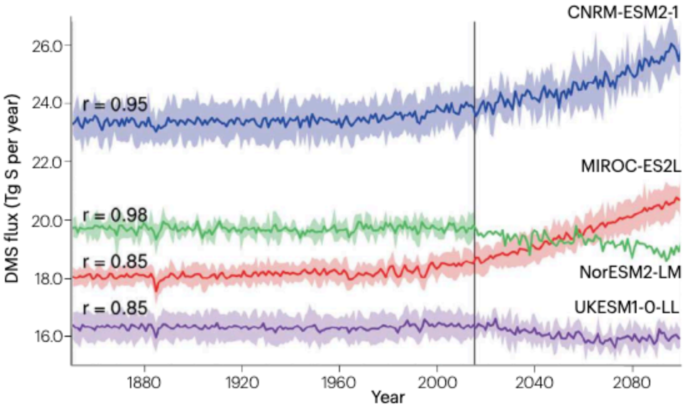

Fig. 6 | Future projections of global dimethylsulfide flux. Time series of annual global dimethylsulfide (DMS) flux (Tg S per year) from 1850 to 2100, showing ensemble mean (thick line) ± 2 standard deviations (shaded envelopes), from four different CMIP6 models (CNRM-ESM2-1, MIROC-ES2L, NorESM2-LM and UKESM1-0-LL). The Earth System Models (ESMs) here use either empirical parameterizations to compute DMS from chlorophyll and other key variables such as mixed layer depth (MIROC-ES2L and UKESM1-0-LL) or prognostic DMS models that include marine biota and parameterizations of key processes that control DMS release (CNRM-ESM2-1 and NorESM2-LM). The Pearson correlation coefficient indicates the agreement between the modelled DMS fluxes (shown) and model DMS surface seawater concentrations (not shown) for each ESM run. High correlation values indicate that DMS concentrations are the primary determinant of DMS fluxes in comparison to other drivers. Figure adapted from ref. 150, CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

in the sub-Arctic North Pacific[220,221]. There is debate as to whether DMS emission changes arising during iron fertilization would be sufficient to impact the regional radiative balance[222–224]. For the Southern Ocean, an assumed average 10% increase in DMS concentrations over the course of a month-long iron addition experiment in the austral summer would result in a small (0.005 °C) decrease in global average annual temperature[223]. The large uncertainties and limited understanding of DMS biogeochemistry[202], emissions and climate effects[2] and the risks of unexpected perturbations and imbalance in the regional energy budget[223] add to the uncertainties associated with geoengineering strategies such as iron addition.

References

1. Charlson, R. J., Lovelock, J. E., Andreae, M. O. & Warren, S. G. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature* **326**, 655–661 (1987).
   Hypothesized the bio-regulation of climate via effect of temperature and sunlight on DMS production.
2. Mahajan, A. S. et al. Quantifying the impacts of an updated global dimethyl sulfide climatology on cloud microphysics and aerosol radiative forcing. *J. Geophys. Res. Atmos.* **120**, 2524–2536 (2015).
3. Fiddes, S. L., Woodhouse, M. T., Nicholls, Z., Lane, T. P. & Schofield, R. Cloud, precipitation and radiation responses to large perturbations in global dimethyl sulfide. *Atmos. Chem. Phys.* **18**, 10177–10198 (2018).
4. Shaw, G. E. Bio-controlled thermostasis involving the sulfur cycle. *Clim. Change* **5**, 297–303 (1983).
5. Ayers, G. & Cainey, J. The CLAW hypothesis: a review of the major developments. *Environ. Chem.* **4**, 366–374 (2007).
6. Meskhidze, N. & Nenes, A. Phytoplankton and cloudiness in the Southern Ocean. *Science* **314**, 1419–1423 (2006).
7. Twohy, C. H. & Anderson, J. R. Droplet nuclei in non-precipitating clouds: composition and size matter. *Environ. Res. Lett.* **3**, 045002 (2008).
8. Bigg, E. K. Sources, nature and influence on climate of marine airborne particles. *Environ. Chem.* **4**, 155–161 (2007).
9. Vallina, S. M., Simo, R. & Manizza, M. Weak response of oceanic dimethylsulfide to upper mixing shoaling induced by global warming. *Proc. Natl Acad. Sci. USA* **104**, 16004–16009 (2007).
10. Woodhouse, M. T. et al. Low sensitivity of cloud condensation nuclei to changes in the sea–air flux of dimethyl-sulphide. *Atmos. Chem. Phys.* **10**, 7545–7559 (2010).
11. Quinn, P. K. & Bates, T. S. The case against climate regulation via oceanic phytoplankton sulphur emissions. *Nature* **480**, 51–56 (2011).
    DMS control over climate brought into question.
12. Mansour, K. et al. Linking marine biological activity to aerosol chemical composition and cloud-relevant properties over the North Atlantic Ocean. *J. Geophys. Res. Atmos.* **125**, e2019JD032246 (2020).
13. McCoy, I. L. et al. Influences of recent particle formation on Southern Ocean aerosol variability and low cloud properties. *J. Geophys. Res. Atmos.* **126**, e2020JD033529 (2021).
14. Sanchez, K. J. et al. Substantial seasonal contribution of observed biogenic sulfate particles to cloud condensation nuclei. *Sci. Rep.* **8**, 3235 (2018).
    New measurements of atmospheric aerosols show importance of algae-derived DMS for CCN in the North Atlantic.
15. Quinn, P. et al. Seasonal variations in western North Atlantic remote marine aerosol properties. *J. Geophys. Res. Atmos.* **124**, 14240–14261 (2019).
16. Saliba, G. et al. Seasonal differences and variability of concentrations, chemical composition, and cloud condensation nuclei of marine aerosol over the North Atlantic. *J. Geophys. Res. Atmos.* **125**, e2020JD033145 (2020).
17. Carslaw, K. S. et al. Large contribution of natural aerosols to uncertainty in indirect forcing. *Nature* **503**, 67–71 (2013).
    Evidence of large contribution of DMS-derived aerosols to uncertainty in indirect forcing.
18. Fung, K. M. et al. Exploring dimethyl sulfide (DMS) oxidation and implications for global aerosol radiative forcing. *Atmos. Chem. Phys.* **22**, 1549–1573 (2022).
19. Faloona, I. Sulfur processing in the marine atmospheric boundary layer: a review and critical assessment of modeling uncertainties. *Atmos. Environ.* **43**, 2841–2854 (2009).
20. Chen, Q., Sherwen, T., Evans, M. & Alexander, B. DMS oxidation and sulfur aerosol formation in the marine troposphere: a focus on reactive halogen and multiphase chemistry. *Atmos. Chem, Phys.* **18**, 13617–13637 (2018).
21. Thomas, M. A. et al. Quantification of DMS aerosol–cloud–climate interactions using the ECHAM5-HAMMOZ model in a current climate scenario. *Atmos. Chem. Phys.* **10**, 7425–7438 (2010).
22. Etminan, M., Myhre, G., Highwood, E. & Shine, K. Radiative forcing of carbon dioxide, methane, and nitrous oxide: a significant revision of the methane radiative forcing. *Geophys. Res. Lett.* **43**, 12614–12623 (2016).
23. Lana, A. et al. An updated climatology of surface dimethlysulfide concentrations and emission fluxes in the global ocean. *Glob. Biogeochem. Cycles* **25**, GB1004 (2011).
    Updated global DMS climatology.
24. Galí, M., Levasseur, M., Devred, E., Simó, R. & Babin, M. Sea-surface dimethylsulfide (DMS) concentration from satellite data at global and regional scales. *Biogeosciences* **15**, 3497–3519 (2018).
25. Wang, W.-L. et al. Global ocean dimethyl sulfide climatology estimated from observations and an artificial neural network. *Biogeosciences* **17**, 5335–5354 (2020).
26. Schaefer, H., Myronova, N. & Boden, R. Microbial degradation of dimethylsulphide and related C1-sulphur compounds: organisms and pathways controlling fluxes of sulphur in the biosphere. *J. Exp. Bot.* **61**, 315–334 (2010).
27. Brimblecombe, P. & Shooter, D. Photo-oxidation of dimethylsulphide in aqueous solution. *Mar. Chem.* **19**, 343–353 (1986).
28. Brimblecombe, P. *Treatise on Geo77chemistry: Second Edition* 559–591 (Elsevier Inc., 2013).
29. Kiene, R. P., Linn, L. J. & Bruton, J. A. New and important roles for DMSP in marine microbial communities. *J. Sea Res.* **43**, 209–224 (2000).
30. Curson, A. R. J., Todd, J. D., Sullivan, M. J. & Johnston, A. W. B. Catabolism of dimethylsulphoniopropionate: microorganisms, enzymes and genes. *Nat. Rev. Microbiol.* **9**, 849 (2011).
31. Galí, M., Devred, E., Levasseur, M., Royer, S.-J. & Babin, M. A remote sensing algorithm for planktonic dimethylsulfoniopropionate (DMSP) and an analysis of global patterns. *Remote Sens. Environ.* **171**, 171–184 (2015).
32. van Duyl, F. C., Gieskes, W. W., Kop, A. J. & Lewis, W. E. Biological control of short-term variations in the concentration of DMSP and DMS during a Phaeocystis spring bloom. *J. Sea Res.* **40**, 221–231 (1998).
33. Speeckaert, G., Borges, A. V., Champenois, W., Royer, C. & Gypens, N. Annual cycle of dimethylsulfoniopropionate (DMSP) and dimethylsulfoxide (DMSO) related to phytoplankton succession in the Southern North Sea. *Sci. Total Environ.* **622**, 362–372 (2018).
34. Kiene, R. P. et al. Unprecedented DMSP concentrations in a massive Dinoflagellate bloom in Monterey Bay, CA. *Geophys. Res. Lett.* **46**, 12279–12288 (2019).
35. Williams, B. T. et al. Bacteria are important dimethylsulfoniopropionate producers in coastal sediments. *Nat. Microbiol.* https://doi.org/10.1038/s41564-019-0527-1 (2019).
36. Van Bergeijk, S., Schönefeldt, K., Stal, L. & Huisman, J. Production and consumption of dimethylsulfide (DMS) and dimethylsulfoniopropionate (DMSP) in a diatom-dominated intertidal sediment. *Mar. Ecol. Prog. Ser.* **231**, 37–46 (2002).
37. Zheng, Y. et al. Bacteria are important dimethylsulfoniopropionate producers in marine aphotic and high-pressure environments. *Nat. Commun.* **11**, 4658 (2020).
38. Trevena, A. J. & Jones, G. B. Dimethylsulphide and dimethylsulphoniopropionate in Antarctic sea ice and their release during sea ice melting. *Mar. Chem.* **98**, 210–222 (2006).
39. Raina, J.-B. et al. DMSP biosynthesis by an animal and its role in coral thermal stress response. *Nature* **502**, 677–680 (2013).
40. Tapiolas, D. M., Raina, J.-B., Lutz, A., Willis, B. L. & Motti, C. A. Direct measurement of dimethylsulfoniopropionate (DMSP) in reef-building corals using quantitative nuclear magnetic resonance (qNMR) spectroscopy. *J. Exp. Mar. Biol. Ecol.* **443**, 85–89 (2013).
41. Burdett, H. L., Hatton, A. D. & Kamenos, N. A. Coralline algae as a globally significant pool of marine dimethylated sulfur. *Glob. Biogeochem. Cycles* **29**, 1845–1853 (2015).
42. Deschaseaux, E., Jones, G. & Swan, H. Dimethylated sulfur compounds in coral-reef ecosystems. *Environ. Chem.* **13**, 239–251 (2015).
43. Swan, H. B. et al. Dimethyl sulfide and other biogenic volatile organic compound emissions from branching coral and reef seawater: potential sources of secondary aerosol over the Great Barrier Reef. *J. Atmos. Chem.* **73**, 303–328 (2016).
44. Van Alstyne, K. L. The distribution of DMSP in green macroalgae from northern New Zealand, eastern Australia and southern Tasmania. *J. Mar. Biol. Assoc. UK* **88**, 799–805 (2008).
45. Otte, M. L. & Morris, J. T. Dimethylsulphoniopropionate (DMSP) in *Spartina alterniflora* Loisel. *Aquat. Bot.* **48**, 239–259 (1994).
46. Kocsis, M. G. et al. Dimethylsulfoniopropionate biosynthesis in *Spartina alterniflora* 1: evidence that *S*-methylmethionine and dimethylsulfoniopropylamine are intermediates. *Plant Physiol.* **117**, 273–281 (1998).
47. Fiddes, S. L., Woodhouse, M. T., Lane, T. P. & Schofield, R. Coral-reef-derived dimethyl sulfide and the climatic impact of the loss of coral reefs. *Atmos. Chem. Phys.* **21**, 5883–5903 (2021).
48. Sunda, W., Kieber, D. J., Kiene, R. P. & Huntsman, S. An antioxidant function for DMSP and DMS in marine algae. *Nature* **418**, 317–320 (2002).
    Evidence that DMSP, DMS and DMSO may serve as a cellular antioxidant system.
49. Stefels, J. et al. The analysis of dimethylsulfide and dimethylsulfoniopropionate in sea ice: dry-crushing and melting using stable isotope additions. *Mar. Chem.* **128–129**, 34–43 (2011).
50. Stefels, J. Physiological aspects of the production and conversion of DMSP in marine algae and higher plants. *J. Sea Res.* **43**, 183–197 (2000).
51. Gardner, S. G., Raina, J.-B., Ralph, P. J. & Petrou, K. Reactive oxygen species (ROS) and dimethylated sulphur compounds in coral explants under acute thermal stress. *J. Exp. Biol.* https://doi.org/10.1242/jeb.153049 (2017).
52. Hopkins, F. E., Bell, T. G., Yang, M., Suggett, D. J. & Steinke, M. Air exposure of coral is a significant source of dimethylsulfide (DMS) to the atmosphere. *Sci. Rep.* **6**, 36031 (2016).
53. Deschaseaux, E. S. et al. Effects of environmental factors on dimethylated sulfur compounds and their potential role in the antioxidant system of the coral holobiont. *Limnol. Oceanogr.* **59**, 758–768 (2014).

54. Stefels, J., Steinke, M., Turner, S., Malin, G. & Belviso, S. Environmental constraints on the production and removal of the climatically active gas dimethylsulphide (DMS) and implications for ecosystem modelling. *Biogeochemistry* **83**, 245–275 (2007).
55. Keller, M. D., Bellows, W. K. & Guillard, R. R. L. in *Biogenic Sulfur in the Environment* (eds Cooper, W. J. & Saltzman, E. S.) Ch. 11 (American Chemical Society, 1989).
56. Curson, A. R. J. et al. DSYB catalyses the key step of dimethylsulfoniopropionate biosynthesis in many phytoplankton. *Nat. Microbiol.* https://doi.org/10.1038/s41564-018-0119-5 (2018).
DSYB enzyme, which controls DMSP synthesis, identified in many phytoplankton and corals.
57. Todd, J. et al. Mechanistic insight into DsyB/DSYB, key enzymes in marine dimethylsulfoniopropionate synthesis. Preprint at *Res. Sq.* https://doi.org/10.21203/rs.3.rs-454893/v1 (2021).
58. Bullock, H. A., Luo, H. & Whitman, W. B. Evolution of dimethylsulfoniopropionate metabolism in marine phytoplankton and bacteria. *Front. Microbiol.* https://doi.org/10.3389/fmicb.2017.00637 (2017).
59. McParland, E. L., Lee, M. D., Webb, E. A., Alexander, H. & Levine, N. M. DMSP synthesis genes distinguish two types of DMSP producer phenotypes. *Environ. Microbiol.* **23**, 1656–1669 (2021).
60. Kageyama, H., Tanaka, Y., Shibata, A., Waditee-Sirisattha, R. & Takabe, T. Dimethylsulfoniopropionate biosynthesis in a diatom *Thalassiosira pseudonana*: identification of a gene encoding MTHB-methyltransferase. *Arch. Biochem. Biophys.* **645**, 100–106 (2018).
61. Otte, M. L., Wilson, G., Morris, J. T. & Moran, B. M. Dimethylsulphoniopropionate (DMSP) and related compounds in higher plants. *J. Exp. Bot.* **55**, 1919–1925 (2004).
62. Liao, C. & Seebeck, F. P. In vitro reconstitution of bacterial DMSP biosynthesis. *Angew. Chem.* **131**, 3591–3594 (2019).
63. Kitaguchi, H., Uchida, A. & Ishida, Y. Purification and characterization of L-methionine decarboxylase from *Crypthecodinium cohnii*. *Fish. Sci.* **65**, 613–617 (1999).
64. Wolfe, G. V. & Steinke, M. Grazing-activated production of dimethyl sulfide (DMS) by two clones of *Emiliania huxleyi*. *Limnol. Oceanogr.* **41**, 1151–1160 (1996).
65. Archer, S., Stelfox-Widdicombe, C., Malin, G. & Burkill, P. Is dimethyl sulphide production related to microzooplankton herbivory in the southern North Sea? *J. Plankton Res.* **25**, 235–242 (2003).
66. Malin, G., Wilson, W. H., Bratbak, G., Liss, P. S. & Mann, N. H. Elevated production of dimethyl sulphide resulting from viral infection of cultures of *Phaeocystis pouchetii*. *Limnol. Oceanogr.* **43**, 1389–1393 (1998).
67. Evans, C. et al. The relative significance of viral lysis and microzooplankton grazing as pathways of dimethylsulfoniopropionate (DMSP) cleavage: an *Emiliania huxleyi* culture study. *Limnol. Oceanogr.* **52**, 1036–1045 (2007).
68. Kwint, R. L. & Kramer, K. J. DMS production by plankton communities. *Mar. Ecol. Prog. Ser.* **121**, 227–237 (1995).
69. Laroche, D. et al. DMSP synthesis and exudation in phytoplankton: a modeling approach. *Mar. Ecol. Prog. Ser.* **180**, 37–49 (1999).
70. Kiene, R. P. & Linn, L. J. The fate of dissolved dimethylsulfoniopropionate (DMSP) in seawater: tracer studies using 35S-DMSP. *Geochim. Cosmochim. Acta* **64**, 2797–2810 (2000).
71. Moran, M. A., Reisch, C. R., Kiene, R. P. & Whitman, W. B. Genomic insights into bacterial DMSP transformations. *Annu. Rev. Mar. Sci.* **4**, 523–542 (2012).
72. Simó, R. et al. The quantitative role of microzooplankton grazing in dimethylsulfide (DMS) production in the NW Mediterranean. *Biogeochemistry* **141**, 125–142 (2018).
73. Wolfe, G. V., Steinke, M. & Kirst, G. O. Grazing-activated chemical defence in a unicellular marine alga. *Nature* **387**, 894–897 (1997).
74. Darroch, L. J. et al. Effect of short-term light- and UV-stress on DMSP, DMS, and DMSP lyase activity in *Emiliania huxleyi*. *Aquat. Microb. Ecol.* **74**, 173–185 (2015).
75. Alcolombri, U. et al. Identification of the algal dimethyl sulfide-releasing enzyme: a missing link in the marine sulfur cycle. *Science* **348**, 1466–1469 (2015).
76. Stefels, J., Gieskes, W. W. C. & Dijkhuizen, L. in *Biological and Environmental Chemistry of DMSP and Related Sulfonium Compounds* (eds Visscher, P. T., Kiene, R. P., Keller, M. D. & Kirst, G. O.) (Plenum, 1996).
77. Steinke, M., Daniel, C. & Kirst, G. O. in *Biological and Environmental Chemistry of DMSP and Related Sulfonium Compounds* (eds Visscher, P. T., Kiene, R. P., Keller, M. D. & Kirst, G. O.) (Plenum, 1996).
78. Steinke, M., Wolfe, G. V. & Kirst, G. O. Partial characterisation of dimethylsulfoniopropionate (DMSP) lyase isozymes in 6 strains of *Emiliania huxleyi*. *Mar. Ecol. Prog. Ser.* **175**, 215–225 (1998).
79. Steinke, M., Stefels, J. & Stamhuis, E. Dimethyl sulfide triggers search behavior in copepods. *Limnol. Oceanogr.* **51**, 1925–1930 (2006).
80. Breckels, M., Bode, N., Codling, E. & Steinke, M. Effect of grazing-mediated dimethyl sulfide (DMS) production on the swimming behavior of the copepod *Calanus helgolandicus*. *Mar. Drugs* **11**, 2486 (2013).
81. Todd, J. D. et al. Structural and regulatory genes required to make the gas dimethyl sulfide in bacteria. *Science* **315**, 666–669 (2007).
82. Curson, A. R. J., Rogers, R., Todd, J. D., Brearley, C. A. & Johnston, A. W. B. Molecular genetic analysis of a dimethylsulfoniopropionate lyase that liberates the climate-changing gas dimethylsulfide in several marine α-proteobacteria and *Rhodobacter sphaeroides*. *Environ. Microbiol.* **10**, 757–767 (2008).
83. Todd, J. D. et al. DddQ, a novel, cupin-containing, dimethylsulfoniopropionate lyase in marine roseobacters and in uncultured marine bacteria. *Environ. Microbiol.* **13**, 427–438 (2011).
84. Todd, J. D., Kirkwood, M., Newton-Payne, S. & Johnston, A. W. DddW, a third DMSP lyase in a model Roseobacter marine bacterium, *Ruegeria pomeroyi* DSS-3. *ISME J.* **6**, 223–226 (2012).
85. Curson, A. R., Sullivan, M. J., Todd, J. D. & Johnston, A. W. DddY, a periplasmic dimethylsulfoniopropionate lyase found in taxonomically diverse species of Proteobacteria. *ISME J.* **5**, 1191–1200 (2011).
86. Sun, J. et al. The abundant marine bacterium *Pelagibacter* simultaneously catabolizes dimethylsulfoniopropionate to the gases dimethyl sulfide and methanethiol. *Nat. Microbiol.* **1**, 16065 (2016).
87. Todd, J. D., Curson, A. R. J., Dupont, C. L., Nicholson, P. & Johnston, A. W. B. The dddP gene, encoding a novel enzyme that converts dimethylsulfoniopropionate into dimethyl sulfide, is widespread in ocean metagenomes and marine bacteria and also occurs in some Ascomycete fungi. *Environ. Microbiol.* **11**, 1376–1385 (2009).
Novel gene *dddP* identified in bacteria for conversion of DMSP to DMS.
88. Li, C.-Y. et al. A novel ATP dependent dimethylsulfoniopropionate lyase in bacteria that releases dimethyl sulfide and acryloyl-CoA. *eLife* **10**, e64045 (2021).
89. Liu, J. et al. Novel insights into bacterial dimethylsulfoniopropionate catabolism in the East China Sea. *Front. Microbiol.* **9**, 3206 (2018).
90. Lee, P. A. & De Mora, S. J. Intracellular dimethylsulfoxide (DMSO) in unicellular marine algae: speculations on its origin and possible biological role. *J. Phycol.* **35**, 8–18 (1999).
91. Andreae, M. O. Dimethylsulfoxide in marine and freshwaters. *Limnol. Oceanogr.* **25**, 1054–1063 (1980).
92. Thume, K. et al. The metabolite dimethylsulfoxonium propionate extends the marine organosulfur cycle. *Nature* **563**, 412–415 (2018).
93. Dixon, J. L., Hopkins, F. E., Stephens, J. A. & Schäfer, H. Seasonal changes in microbial dissolved organic sulfur transformations in coastal waters. *Microorganisms* **8**, 337 (2020).
94. Spiese, C. E., Kieber, D. J., Nomura, C. T. & Kiene, R. P. Reduction of dimethylsulfoxide to dimethylsulfide by marine phytoplankton. *Limnol. Oceanogr.* **54**, 560–570 (2009).
95. McCrindle, S. L., Kappler, U. & McEwan, A. G. Microbial dimethylsulfoxide and trimethylamine-N-oxide respiration. *Adv. Microb. Physiol.* **50**, 147–198 (2005).
96. Simó, R., Grimalt, J. O. & Albaiges, J. Dissolved dimethylsulphide, dimethylsulphoniopropionate and dimethylsulphoxide in western Mediterranean waters. *Deep Sea Res. II* **44**, 929–950 (1997).
97. Kiene, R. P. & Gerard, G. Determination of trace levels of dimethylsulfoxide (DMSO) in seawater and rainwater. *Mar. Chem.* **47**, 1–12 (1994).
98. Hatton, A., Malin, G., Turner, S. & Liss, P. in *Biological and Environmental Chemistry of DMSP and Related Sulfonium Compounds* 405–412 (Springer, 1996).
99. Carrión, O. et al. Methanethiol-dependent dimethylsulfide production in soil environments. *ISME J.* **11**, 2379–2390 (2017).
100. Carrión, O. et al. A novel pathway producing dimethylsulphide in bacteria is widespread in soil environments. *Nat. Commun.* **6**, 6579 (2015).
101. Pinhassi, J. et al. Dimethylsulfoniopropionate turnover is linked to the composition and dynamics of the bacterioplankton assemblage during a microcosm phytoplankton bloom. *Appl. Environ. Microbiol.* **71**, 7650–7660 (2005).
102. Howard, E. C., Sun, S., Biers, E. J. & Moran, M. A. Abundant and diverse bacteria involved in DMSP degradation in marine surface waters. *Environ. Microbiol.* **10**, 2397–2410 (2008).
103. Landa, M. et al. Sulfur metabolites that facilitate oceanic phytoplankton–bacteria carbon flux. *ISME J.* **13**, 2536–2550 (2019).
104. Todd, J. D., Curson, A. R., Sullivan, M. J., Kirkwood, M. & Johnston, A. W. The *Ruegeria pomeroyi* acuI gene has a role in DMSP catabolism and resembles yhdH of *E. coli* and other bacteria in conferring resistance to acrylate. *PLoS ONE* **7**, e35947 (2012).
105. Nakamura, H., Fujimaki, K., Sampei, O. & Murai, A. Gonyol: methionine-induced sulfonium accumulation in a dinoflagellate *Gonyaulax polyedra*. *Tetrahedron Lett.* **34**, 8481–8484 (1993).
106. Nakamura, H. Synthesis of (±)-gonyauline, an endogenous substance shortening the period of circadian rhythm in the unicellular alga *Gonyaulax polyedra*. *J. Chem. Soc. Perkin Trans.* **1**, 3219–3220 (1990).
107. Cosquer, A. et al. Nanomolar levels of dimethylsulfoniopropionate, dimethylsulfonioacetate, and glycine betaine are sufficient to confer osmoprotection to *Escherichia coli*. *Appl. Environ. Microbiol.* **65**, 3304–3311 (1999).
108. Gebser, B., Thume, K., Steinke, M. & Pohnert, G. Phytoplankton-derived zwitterionic gonyol and dimethylsulfonioacetate interfere with microbial dimethylsulfoniopropionate sulfur cycling. *MicrobiologyOpen* **9**, e1014 (2020).
109. Burkhardt, I., Lauterbach, L., Brock, N. L. & Dickschat, J. S. Chemical differentiation of three DMSP lyases from the marine *Roseobacter* group. *Org. Biomol. Chem.* **15**, 4432–4439 (2017).
110. Gregory, G. J., Boas, K. E., Boyd, E. F. & Stabb, E. V. The organosulfur compound dimethylsulfoniopropionate (DMSP) is utilized as an osmoprotectant by *Vibrio* species. *Appl. Environ. Microbiol.* **87**, e02235-20 (2021).
111. Theseira, A. M., Nielsen, D. A. & Petrou, K. Uptake of dimethylsulphoniopropionate (DMSP) reduces free reactive oxygen species (ROS) during late exponential growth in the diatom *Thalassiosira weissflogii* grown under three salinities. *Mar. Biol.* **167**, 127 (2020).
112. Archer, S. D., Widdicombe, C. E., Tarran, G. A., Rees, A. P. & Burkill, P. H. Production and turnover of particulate dimethylsulphoniopropionate during a Coccolithophore bloom in the northern North Sea. *Aquat. Microb. Ecol.* **24**, 225–241 (2001).
113. Saló, V., Simó, R., Vila-Costa, M. & Calbet, A. Sulfur assimilation by *Oxyrrhis marina* feeding on a 35S-DMSP-labelled prey. *Environ. Microbiol.* **11**, 3063–3072 (2009).

114. Kappler, U. & Schäfer, H. *The Metal-Driven Biogeochemistry of Gaseous Compounds in the Environment* 279–313 (Springer, 2014).
115. Toole, D. A., Kieber, D. J., Kiene, R. P., Siegel, D. A. & Nelson, N. B. Photolysis and the dimethylsulfide (DMS) summer paradox in the Sargasso Sea. *Limnol. Oceanogr.* **48**, 1088–1100 (2003).
116. Toole, D., Slezak, D., Kiene, R., Kieber, D. & Siegel, D. Effects of solar radiation on dimethylsulfide cycling in the western Atlantic Ocean. *Deep Sea Res. Part I Oceanogr. Res. Pap.* **53**, 136–153 (2006).
117. Kieber, D. J., Jiao, J. F., Kiene, R. P. & Bates, T. S. Impact of dimethylsulfide photochemistry on methyl sulfur cycling in the equatorial Pacific Ocean. *J. Geophys. Res. Oceans* **101**, 3715–3722 (1996).
118. Galí, M., Devred, E., Pérez, G. L., Kieber, D. J. & Simó, R. Global ocean dimethylsulfide photolysis rates quantified with a spectrally and vertically resolved model. *Limnol. Oceanogr. Lett.* https://doi.org/10.31223/X5VM0C (2022).
119. Simo, R., Hatton, A. D., Malin, G. & Liss, P. S. Particulate dimethyl sulphoxide in seawater: production by microplankton. *Mar. Ecol. Prog. Ser.* **167**, 291–296 (1998).
120. del Valle, D. A., Kieber, D. J., John, B. & Kiene, R. P. Light-stimulated production of dissolved DMSO by a particle-associated process in the Ross Sea, Antarctica. *Limnol. Oceanogr.* **52**, 2456–2466 (2007).
121. del Valle, D. A., Kieber, D. J., Toole, D. A., Bisgrove, J. & Kiene, R. P. Dissolved DMSO production via biological and photochemical oxidation of dissolved DMS in the Ross Sea, Antarctica. *Deep Sea Res. Part I Oceanogr. Res. Pap.* **56**, 166–177 (2009).
122. Zeyer, J., Eicher, P., Wakeham, S. G. & Schwarzenbach, R. P. Oxidation of dimethyl sulfide to dimethyl sulfoxide by phototrophic purple bacteria. *Appl. Environ. Microbiol.* **53**, 2026–2032 (1987).
123. Vogt, C., Rabenstein, A., Rethmeier, J. & Fischer, U. Dimethyl sulphoxide reduction with reduced sulphur compounds as electron donors by anoxygenic phototrophic bacteria. *Microbiology* **143**, 767–773 (1997).
124. Hanlon, S. P., Toh, T. H., Solomon, P. S., Holt, R. A. & Mcewan, A. G. Dimethylsulfide: acceptor oxidoreductase from *Rhodobacter sulfidophilus*: the purified enzyme contains b-type Haem and a Pterin molybdenum cofactor. *Eur. J. Biochem.* **239**, 391–396 (1996).
125. Fuse, H., Takimura, O., Murakami, K., Yamaoka, Y. & Omori, T. Utilization of dimethyl sulfide as a sulfur source with the aid of light by *Marinobacterium* sp. strain DMS-S1. *Appl. Environ. Microbiol.* **66**, 5527–5532 (2000).
126. Omori, T., Saiki, Y., Kasuga, K. & Kodama, T. Desulfurization of alkyl and aromatic sulfides and sulfonates by dibenzothiophene-desulfurizing *Rhodococcus* sp. strain SY1. *Biosci. Biotechnol. Biochem.* **59**, 1195–1198 (1995).
127. Sorokin, D. Y., Jones, B. E. & Kuenen, J. G. An obligate methylotrophic, methane-oxidizing *Methylomicrobium* species from a highly alkaline environment. *Extremophiles* **4**, 145–155 (2000).
128. De Bont, J., Van Dijken, J. & Harder, W. Dimethyl sulphoxide and dimethyl sulphide as a carbon, sulphur and energy source for growth of *Hyphomicrobium* S. *Microbiology* **127**, 315–323 (1981).
129. Boden, R. et al. Purification and characterization of dimethylsulfide monooxygenase from *Hyphomicrobium sulfonivorans*. *J. Bacteriol.* **193**, 1250–1258 (2011).
130. Song, D. et al. Metagenomic insights into the cycling of dimethylsulfoniopropionate and related molecules in the Eastern China Marginal Seas. *Front. Microbiol.* **11**, 157 (2020).
131. Suylen, G., Large, P., Van Dijken, J. & Kuenen, J. Methyl mercaptan oxidase, a key enzyme in the metabolism of methylated sulphur compounds by *Hyphomicrobium* EG. *Microbiology* **133**, 2989–2997 (1987).
132. Eyice, Ö. et al. Bacterial SBP56 identified as a Cu-dependent methanethiol oxidase widely distributed in the biosphere. *ISME J.* **12**, 145–160 (2018).
133. Anthony, C. *The Biochemistry of Methylotrophs* Vol. 439 (Academic Press, 1982).
134. Neufeld, J. D., Boden, R., Moussard, H., Schafer, H. & Murrell, J. C. Substrate-specific clades of active marine methylotrophs associated with a phytoplankton bloom in a temperate coastal environment. *Appl. Environ. Microbiol.* **74**, 7321–7328 (2008).
135. Pesant, S. et al. Open science resources for the discovery and analysis of Tara Oceans data. *Sci. Data* **2**, 150023 (2015).
136. Vorobev, A. et al. Transcriptome reconstruction and functional analysis of eukaryotic marine plankton communities via high-throughput metagenomics and metatranscriptomics. *Genome Res.* **30**, 647–659 (2020).
137. Teng, Z.-J. et al. Biogeographic traits of dimethyl sulfide and dimethylsulfoniopropionate cycling in polar oceans. *Microbiome* **9**, 207 (2021).
138. Sun, H. et al. DMSP-producing bacteria are more abundant in the surface microlayer than subsurface seawater of the East China Sea. *Microb. Ecol.* **80**, 350–365 (2020).
139. Li, C.-Y. et al. Mechanistic insights into the key marine dimethylsulfoniopropionate synthesis enzyme DsyB/DSYB. *mLife* **1**, 114–130 (2022).
140. Kettle, A. J. et al. A global database of sea surface dimethylsulfide (DMS) measurements and a procedure to predict sea surface DMS as a function of latitude, longitude, and month. *Glob. Biogeochem. Cycles* **13**, 399–444 (1999).
141. Bell, T. G. et al. Estimation of bubble-mediated air–sea gas exchange from concurrent DMS and CO_2 transfer velocities at intermediate–high wind speeds. *Atmos. Chem. Phys.* **17**, 9019–9033 (2017).
142. Nightingale, P. D. et al. In situ evaluation of air–sea gas exchange parameterizations using novel conservative and volatile tracers. *Glob. Biogeochem. Cycles* **14**, 373–387 (2000).
143. Huebert, B. J. et al. Measurement of the sea–air DMS flux and transfer velocity using eddy correlation. *Geophys. Res. Lett.* https://doi.org/10.1029/2004GL021567 (2004).
First eddy correlation measurement of DMS sea–air fluxes.
144. Marandino, C. A., De Bruyn, W. J., Miller, S. D. & Saltzman, E. S. Eddy correlation measurements of the air/sea flux of dimethylsulfide over the North Pacific Ocean. *J. Geophys. Res. Atmos.* https://doi.org/10.1029/2006JD007293 (2007).
145. Bell, T. G. et al. Dimethylsulfide gas transfer coefficients from algal blooms in the Southern Ocean. *Atmos. Chem. Phys.* **15**, 1783–1794 (2015).
146. Goddijn-Murphy, L., Woolf, D. K. & Marandino, C. Space-based retrievals of air–sea gas transfer velocities using altimeters: calibration for dimethyl sulfide. *J. Geophys. Res. Oceans* https://doi.org/10.1029/2011JC007535 (2012).
147. Blomquist, B. W. et al. Wind speed and sea state dependencies of air–sea gas transfer: results from the high wind speed gas exchange study (HiWinGS). *J. Geophys. Res. Ocean.* **122**, 8034–8062 (2017).
148. Liss, P. & Merlivat, L. in *The Role of Air–Sea Exchange in Geochemical Cycling* (ed. Buat-Menard, P.) (D Reidel, 1986).
149. Wanninkhof, R. Relationship between wind speed and gas exchange over the ocean revisited. *Limnol. Oceanogr. Methods* **12**, 351–362 (2014).
150. Bock, J. et al. Evaluation of ocean dimethylsulfide concentration and emission in CMIP6 models. *Biogeosciences* **18**, 3823–3860 (2021).
151. Hulswar, S. et al. Third revision of the global surface seawater dimethyl sulfide climatology (DMS-Rev3). *Earth Syst. Sci. Data* **14**, 2963–2987 (2022).
152. Simó, R. & Dachs, J. Global ocean emission of dimethylsulfide predicted from biogeophysical data. *Global Biogeochem. Cycles* https://doi.org/10.1029/2001GB001829 (2002).
153. Vallina, S. M. & Simo, R. Strong relationship between DMS and the solar radiation dose over the global surface ocean. *Science* **315**, 506–508 (2007).
154. Humphries, G. R., Deal, C. J., Elliott, S. & Huettmann, F. Spatial predictions of sea surface dimethylsulfide concentrations in the High Arctic. *Biogeochemistry* **110**, 287–301 (2012).
155. Kloster, S. et al. DMS cycle in the marine ocean–atmosphere system — a global model study. *Biogeosciences* **3**, 29–51 (2006).
156. Nguyen, B. C., Mihalopoulos, N. & Belviso, S. Seasonal variation of atmospheric dimethyl sulphide at Amsterdam Island in the Southern Indian Ocean. *J. Atmos. Chem.* **11**, 123–141 (1990).
157. Ayers, G., Gillett, R., Ivey, J., Schäfer, B. & Gabric, A. Short-term variability in marine atmospheric dimethylsulfide concentration. *Geophys. Res. Lett.* **22**, 2513–2516 (1995).
158. Kouvarakis, G. & Mihalopoulos, N. Seasonal variation of dimethylsulfide in the gas phase and of methanesulfonate and non-sea-salt sulfate in the aerosols phase in the Eastern Mediterranean atmosphere. *Atmos. Environ.* **36**, 929–938 (2002).
159. Gershenzon, M., Davidovits, P., Jayne, J., Kolb, C. & Worsnop, D. Simultaneous uptake of DMS and ozone on water. *J. Phys. Chem. A* **105**, 7031–7036 (2001).
160. Bonifacic, M., Schaefer, K., Moeckel, H. & Asmus, K. Primary steps in the reactions of organic disulfides with hydroxyl radicals in aqueous solution. *J. Phys. Chem.* **79**, 1496–1502 (1975).
161. Boucher, O. et al. DMS atmospheric concentrations and sulphate aerosol indirect radiative forcing: a sensitivity study to the DMS source representation and oxidation. *Atmos. Chem. Phys.* **3**, 49–65 (2003).
162. von Glasow, R. & Crutzen, P. J. Tropospheric halogen chemistry. *Treatise Geochem.* **4**, 347 (2003).
163. Hoffmann, E. H. et al. An advanced modeling study on the impacts and atmospheric implications of multiphase dimethyl sulfide chemistry. *Proc. Natl Acad. Sci. USA* **113**, 11776–11781 (2016).
164. Zhu, L., Nenes, A., Wine, P. H. & Nicovich, J. M. Effects of aqueous organosulfur chemistry on particulate methanesulfonate to non–sea salt sulfate ratios in the marine atmosphere. *J. Geophys. Res. Atmos.* https://doi.org/10.1029/2005JD006326 (2006).
165. Barnes, I., Hjorth, J. & Mihalopoulos, N. Dimethyl sulfide and dimethyl sulfoxide and their oxidation in the atmosphere. *Chem. Rev.* **106**, 940–975 (2006).
166. von Glasow, R. & Crutzen, P. J. Model study of multiphase DMS oxidation with a focus on halogens. *Atmos. Chem. Phys.* **4**, 589–608 (2004).
First comprehensive model study of atmospheric multiphase DMS oxidation.
167. Glasow, R. V., von Kuhlmann, R., Lawrence, M. G., Platt, U. & Crutzen, P. J. Impact of reactive bromine chemistry in the troposphere. *Atmos. Chem. Phys.* **4**, 2481–2497 (2004).
168. Ayers, G. P. & Gras, J. L. Seasonal relationship between cloud condensation nuclei and aerosol methanesulphonate in marine air. *Nature* **353**, 834–835 (1991).
169. Kukui, A., Borissenko, D., Laverdet, G. & Le Bras, G. Gas-phase reactions of OH radicals with dimethyl sulfoxide and methane sulfinic acid using turbulent flow reactor and chemical ionization mass spectrometry. *J. Phys. Chem. A* **107**, 5732–5742 (2003).
170. Lu, Y. et al. A proxy for atmospheric daytime gaseous sulfuric acid concentration in urban Beijing. *Atmos. Chem. Phys.* **19**, 1971–1983 (2019).
171. Facchini, M. C. et al. Important source of marine secondary organic aerosol from biogenic amines. *Environ. Sci. Technol.* **42**, 9116–9121 (2008).
172. Dall'Osto, M. et al. Nitrogenated and aliphatic organic vapors as possible drivers for marine secondary organic aerosol growth. *J. Geophys. Res. Atmos.* **117**, 017522 (2012).
173. Chen, H. & Finlayson-Pitts, B. J. New particle formation from methanesulfonic acid and amines/ammonia as a function of temperature. *Environ. Sci. Technol.* **51**, 243–252 (2017).
174. Hodshire, A. L. et al. The potential role of methanesulfonic acid (MSA) in aerosol formation and growth and the associated radiative forcings. *Atmos. Chem. Phys.* **19**, 3137–3160 (2019).
175. Dawson, M. L. et al. Simplified mechanism for new particle formation from methanesulfonic acid, amines, and water via experiments and ab initio calculations. *Proc. Natl Acad. Sci. USA* **109**, 18719–18724 (2012).

176. Chen, H. et al. New particle formation and growth from methanesulfonic acid, trimethylamine and water. *Phys. Chem. Chem. Phys.* **17**, 13699–13709 (2015).
177. Ning, A. et al. A molecular-scale study on the role of methanesulfinic acid in marine new particle formation. *Atmos. Environ.* **227**, 117378 (2020).
178. Berndt, T. et al. Fast peroxy radical isomerization and OH recycling in the reaction of OH radicals with dimethyl sulfide. *J. Phys. Chem. Lett.* https://doi.org/10.1021/acs.jpclett.9b02567 (2019).
Identification of new and more rapid DMS atmospheric oxidation pathway.
179. Veres, P. R. et al. Global airborne sampling reveals a previously unobserved dimethyl sulfide oxidation mechanism in the marine atmosphere. *Proc. Natl Acad. Sci. USA* **117**, 4505–4510 (2020).
Discovery of major DMS gas-phase oxidation product HPMTF, which could account for>30% of oceanic DMS emissions and strongly influence new particle formation and growth.
180. Bates, T. S. et al. Processes controlling the distribution of aerosol particles in the lower marine boundary layer during the First Aerosol Characterization Experiment (ACE 1). *J. Geophys. Res. Atmos.* **103**, 16369–16383 (1998).
181. Twohy, C. H. et al. Cloud-nucleating particles over the Southern Ocean in a changing climate. *Earths Future* **9**, e2020EF001673 (2021).
182. Sanchez, K. J. et al. Measurement report: cloud processes and the transport of biological emissions affect Southern Ocean particle and cloud condensation nuclei concentrations. *Atmos. Chem. Phys.* **21**, 3427–3446 (2021).
183. Yin, F., Grosjean, D., Flagan, R. C. & Seinfeld, J. H. Photooxidation of dimethyl sulfide and dimethyl disulfide. II: mechanism evaluation. *J. Atmos. Chem.* **11**, 365–399 (1990).
184. Yin, F., Grosjean, D. & Seinfeld, J. H. Photooxidation of dimethyl sulfide and dimethyl disulfide. I: mechanism development. *J. Atmos. Chem.* **11**, 309–364 (1990).
185. Khan, M. A. H. et al. A modelling study of the atmospheric chemistry of DMS using the global model, STOCHEM-CRI. *Atmos. Environ.* **127**, 69–79 (2016).
186. Revell, L. E. et al. The sensitivity of Southern Ocean aerosols and cloud microphysics to sea spray and sulfate aerosol production in the HadGEM3-GA7.1 chemistry–climate model. *Atmos. Chem. Phys.* **19**, 15447–15466 (2019).
187. Wang, S., Maltrud, M., Elliott, S., Cameron-Smith, P. & Jonko, A. Influence of dimethyl sulfide on the carbon cycle and biological production. *Biogeochemistry* **138**, 49–68 (2018).
188. Swan, H. B. The potential for great barrier reef regional climate regulation via dimethylsulfide atmospheric oxidation products. *Front. Mar. Sci.* **9**, 869166 (2022).
189. Bell, T. G. et al. Predictability of seawater DMS during the North Atlantic Aerosol and Marine Ecosystem Study (NAAMES). *Front. Mar. Sci.* https://doi.org/10.3389/fmars.2020.596763 (2021).
Current state-of-the-art approaches for estimating seawater DMS hindered by unrealistic representation of biological processes and poorly predict DMS during episodes of enhanced net production.
190. Halloran, P., Bell, T. & Totterdell, I. Can we trust empirical marine DMS parameterisations within projections of future climate? *Biogeosciences* **7**, 1645–1656 (2010).
191. Elliott, S. Dependence of DMS global sea–air flux distribution on transfer velocity and concentration field type. *J. Geophys. Res. Biogeosci.* **114**, G02001 (2009).
192. Tesdal, J.-E., Christian, J. R., Monahan, A. H. & von Salzen, K. Evaluation of diverse approaches for estimating sea-surface DMS concentration and air–sea exchange at global scale. *Environ. Chem.* **13**, 390–412 (2016).
193. Tesdal, J. E., Christian, J. R., Monahan, A. H. & von Salzen, K. Sensitivity of modelled sulfate aerosol and its radiative effect on climate to ocean DMS concentration and air–sea flux. *Atmos. Chem. Phys.* **16**, 10847–10864 (2016).
194. Galí, M. et al. Diel patterns of oceanic dimethylsulfide (DMS) cycling: microbial and physical drivers. *Glob. Biogeochem. Cycles* **27**, 620–636 (2013).
195. Stefels, J., Dacey, J. W. & Elzenga, J. T. M. In vivo DMSP-biosynthesis measurements using stable-isotope incorporation and proton-transfer-reaction mass spectrometry (PTR-MS). *Limnol. Oceanogr. Methods* **7**, 595–611 (2009).
196. Litchman, E. & Klausmeier, C. A. Trait-based community ecology of phytoplankton. *Annu. Rev. Ecol. Evol. Syst.* **39**, 615–639 (2008).
197. Archer, S. D., Gilbert, F. J., Allen, J. I., Blackford, J. & Nightingale, P. D. Modelling of the seasonal patterns of dimethylsulphide production and fate during 1989 at a site in the North Sea. *Can. J. Fish. Aquat. Sci.* **61**, 765–787 (2004).
198. McParland, E. L. & Levine, N. M. The role of differential DMSP production and community composition in predicting variability of global surface DMSP concentrations. *Limnol. Oceanogr.* **64**, 757–773 (2019).
199. Wang, S., Maltrud, M. E., Burrows, S. M., Elliott, S. M. & Cameron-Smith, P. Impacts of shifts in phytoplankton community on clouds and climate via the sulfur cycle. *Glob. Biogeochem. Cycles* **32**, 1005–1026 (2018).
200. Saltzman, E., De Bruyn, W., Lawler, M., Marandino, C. & McCormick, C. A chemical ionization mass spectrometer for continuous underway shipboard analysis of dimethylsulfide in near-surface seawater. *Ocean. Sci.* **5**, 537–546 (2009).
201. Tortell, P. D. Dissolved gas measurements in oceanic waters made by membrane inlet mass spectrometry. *Limnol. Oceanogr. Methods* **3**, 24–37 (2005).
202. Bell, T. G. et al. Seawater DMS variability during the North Atlantic Aerosol and Marine Ecosystem Study (NAAMES). *Front. Mar. Sci.* **7**, 1200 (2020).
203. Kameyama, S. et al. Equilibrator inlet-proton transfer reaction-mass spectrometry (EI-PTR-MS) for sensitive, high-resolution measurement of dimethyl sulfide dissolved in seawater. *Anal. Chem.* **81**, 9021–9026 (2009).
204. Bolas, C. G. et al. iDirac: a field-portable instrument for long-term autonomous measurements of isoprene and selected VOCs. *Atmos. Meas. Tech.* **13**, 821–838 (2020).
205. Okane, D. et al. High sensitivity monitoring device for onboard measurement of dimethyl sulfide and dimethylsulfoniopropionate in seawater and an oceanic atmosphere. *Anal. Chem.* **91**, 10484–10491 (2019).
206. Leng, G. et al. Automated, high frequency, on-line dimethyl sulfide measurements in natural waters using a novel 'microslug' gas–liquid segmented flow method with chemiluminescence detection. *Talanta* **221**, 121595 (2021).
207. Tang, W. et al. Widespread phytoplankton blooms triggered by 2019–2020 Australian wildfires. *Nature* **597**, 370–375 (2021).
208. McNabb, B. J. & Tortell, P. D. Improved prediction of dimethyl sulfide (DMS) distributions in the northeast subarctic Pacific using machine-learning algorithms. *Biogeosciences* **19**, 1705–1721 (2022).
209. Hopkins, F. E. et al. The impacts of ocean acidification on marine trace gases and the implications for atmospheric chemistry and climate. *R. Soc. Proc. A* **476**, 20190769 (2020).
Review of impacts ocean acidification on DMS production.
210. Bopp, L., Aumont, O., Belviso, S. & Monfray, P. Potential impact of climate change on marine dimethyl sulphide emissions. *Tellus B* **55**, 11–22 (2003).
First model estimate of response of DMS production and flux to climate change.
211. Bopp, L. et al. Will marine dimethyl sulphide emissions amplify of alleviate global warming? A model study. *Can. J. Fish. Aquat. Sci.* **61**, 826–835 (2004).
212. Gabric, A. J., Bo, Q. U., Patricia, M. & Anthony, H. C. The simulated response of dimethylsulfide production in the Arctic Ocean to global warming. *Tellus B* **57**, 391–403 (2005).
213. Kloster, S. et al. Response of dimethylsulfide (DMS) in the ocean and atmosphere to global warming. *J. Geophys. Res.* https://doi.org/10.1029/2006JG000224 (2007).
214. Cameron-Smith, P., Elliott, S., Maltrud, M., Erickson, D. & Wingenter, O. Changes in dimethyl sulfide oceanic distribution due to climate change. *Geophys. Res. Lett.* **38**, L07704 (2011).
215. Menzo, Z., Elliott, S., Hartin, C., Hoffman, F. & Wang, S. Climate change impacts on natural sulfur production: ocean acidification and community shifts. *Atmosphere* **9**, 167 (2018).
216. Six, K. D. et al. Global warming amplified by reduced sulphur fluxes as a result of ocean acidification. *Nat. Clim. Change* **3**, 975 (2013).
217. Schwinger, J. et al. Amplification of global warming through pH dependence of DMS production simulated with a fully coupled Earth system model. *Biogeosciences* **14**, 3633–3648 (2017).
A fully coupled model study demonstrating climate sensitivity to ocean acidification-driven reduction in DMS flux.
218. Boyd, P. W. et al. Experimental strategies to assess the biological ramifications of multiple drivers of global ocean change — a review. *Glob. Change Biol.* **24**, 2239–2261 (2018).
219. GESAMP. *High Level Review of a Wide Range of Proposed Marine Geoengineering Techniques*. Report No. 1020-4873, 144 (2019).
220. Boyd, P. W. et al. Mesoscale iron enrichment experiments 1993–2005: synthesis and future directions. *Science* **315**, 612–617 (2007).
221. Turner, S. M., Harvey, M. J., Law, C. S., Nightingale, P. D. & Liss, P. S. Iron-induced changes in oceanic sulfur biogeochemistry. *Geophys. Res. Lett.* https://doi.org/10.1029/2004GL020296 (2004).
222. Wingenter, O. W., Elliot, S. M. & Blake, D. R. New directions: enhancing the natural sulfur cycle to slow global warming. *Atmos. Environ.* **41**, 7373–7375 (2007).
223. Vogt, M., Vallina, S. & von Glasow, R. New directions: correspondence on 'enhancing the natural cycle to slow global warming'. *Atmos. Environ.* **42**, 4803–4805 (2008).
224. Law, C. S. Predicting and monitoring the effects of large-scale ocean iron fertilization on marine trace gas emissions. *Mar. Ecol. Prog. Ser.* **364**, 283–288 (2008).
225. Lovelock, J. E., Maggs, R. J. & Rasmussen, R. A. Atmospheric dimethyl sulphide and the natural sulphur cycle. *Nature* **237**, 452–453 (1972).
226. Haas, P. The liberation of methyl sulphide by seaweed. *Biochem. J.* **29**, 1297–1299 (1935).
227. Challenger, F. & Simpson, M. I. Studies on biological methylation. Part 12. A precursor of the dimethyl sulphide evolved by *Polysiphonia fastigiata*. Dimethyl-2-carboxyethylsulphonium hydroxide and its salts. *J. Chem. Soc.* **3**, 1591–1597 (1948).
228. Ishida, Y. *Physiological Studies on Evolution of Dimethyl Sulfide from Unicellular Marine Algae*. Dissertation, Kyoto Univ. (1969).
229. Andreae, M. O. Determination of trace quantities of dimethylsulfoxide in aqueous solutions. *Anal. Chem.* **52**, 150–153 (1980).
230. Andreae, M. O. & Raemdonck, H. Dimethyl sulfide in the surface ocean and the marine atmosphere: a global view. *Science* **221**, 744–747 (1983).
231. Dacey, J. W. H., Wakeham, S. G. & Howes, B. L. Henry's law constants for dimethylsulfide in freshwater and seawater. *Geophys. Res. Lett.* **11**, 991–994 (1984).
232. Dacey, J. W. & Wakeham, S. G. Oceanic dimethylsulfide: production during zooplankton grazing on phytoplankton. *Science* **233**, 1314–1316 (1986).
233. Erikson, D. J., Ghan, S. J. & Penner, J. E. Global ocean-to-atmosphere dimethyl sulfide flux. *J. Geophys. Res.* **95**, 7543–7552 (1990).
234. Kiene, R. P. & Bates, T. S. Biological removal of dimethyl sulphide from sea water. *Nature* **345**, 702–705 (1990).
235. Kiene, R. P. Dimethyl sulfide production from dimethylsulfoniopropionate in coastal seawater samples and bacterial cultures. *Appl. Environ. Microbiol.* **56**, 3292–3297 (1990).
236. Ayers, G. P., Ivey, J. P. & Gillett, R. W. Coherence between seasonal cycles of dimethyl sulphide, methanesulphonate and sulphate in marine air. *Nature* **349**, 404–406 (1991).

237. Kiene, R. P. Dynamics of dimethyl sulfide and dimethylsulfoniopropionate in oceanic water samples. *Mar. Chem.* **37**, 29–52 (1992).
238. Bates, T. S. et al. The cycling of sulfur in surface seawater of the northeast Pacific. *J. Geophys. Res. Ocean.* **99**, 7835–7843 (1994).
239. Levasseur, M., Gosselin, M. & Michaud, S. A new source of dimethylsulfide (DMS) for the arctic atmosphere: ice diatoms. *Mar. Biol.* **121**, 381–387 (1994).
240. Hill, R. W., Dacey, J. W. & Krupp, D. A. Dimethylsulfoniopropionate in reef corals. *Bull. Mar. Sci.* **57**, 489–494 (1995).
241. Nevitt, G. A., Veit, R. R. & Kareiva, P. Dimethyl sulphide as a foraging cue for Antarctic procellariiform seabirds. *Nature* **376**, 680 (1995).
242. Zubkov, M. V. et al. Linking the composition of bacterioplankton to rapid turnover of dissolved dimethylsulphoniopropionate in an algal bloom in the North Sea. *Environ. Microbiol.* **3**, 304–311 (2001).
243. Burkhill, P. H. et al. Dimethyl sulphide biogeochemistry within a coccolithophore bloom (DISCO): an overview. *Deep Sea Res. II* **49**, 2863–2885 (2002).
244. Gunson, J. R. et al. Climate sensitivity to ocean dimethylsulphide emissions. *Geophys. Res. Lett.* https://doi.org/10.1029/2005GL024982 (2006).
245. Vogt, M. et al. Dynamics of dimethylsulphoniopropionate and dimethylsulphide under different CO_2 concentrations during a mesocosm experiment. *Biogeosciences* **5**, 407–419 (2008).
246. Hopkins, F. E., Turner, S. M., Nightingale, P. D., Steinke, M. & Liss, P. S. Ocean acidification and marine biogenic trace gas production. *Proc. Natl Acad. Sci. USA* **107**, 760–765 (2010).
247. Archer, S. D. et al. Contrasting responses of DMS and DMSP to ocean acidification in Arctic waters. *Biogeosciences* **10**, 1893–1908 (2013).
    Experimental evidence of DMS sensitivity to ocean acidification in the Arctic.
248. Leaitch, W. R. et al. Dimethyl sulfide control of the clean summertime Arctic aerosol and cloud. *Elem. Sci. Anthr.* **1**, 000017 (2013).
    Evidence of DMS control on Arctic aerosol and cloud processes.
249. Savoca, M. S. & Nevitt, G. A. Evidence that dimethyl sulfide facilitates a tritrophic mutualism between marine primary producers and top predators. *Proc. Natl Acad. Sci. USA* **111**, 4157–4161 (2014).
250. Savoca, M. S., Wohlfeil, M. E., Ebeler, S. E. & Nevitt, G. A. Marine plastic debris emits a keystone infochemical for olfactory foraging seabirds. *Sci. Adv.* https://doi.org/10.1126/sciadv.1600395 (2016).
251. Lidbury, I. et al. A mechanism for bacterial transformation of dimethylsulfide to dimethylsulfoxide: a missing link in the marine organic sulfur cycle. *Environ. Microbiol.* **18**, 2754–2766 (2016).
252. Jackson, R. L., Gabric, A. J., Cropp, R. & Woodhouse, M. T. Dimethylsulfide (DMS), marine biogenic aerosols and the ecophysiology of coral reefs. *Biogeosciences* **17**, 2181–2204 (2020).
253. Swan, H. B., Jones, G. B., Deschaseaux, E. S. & Eyre, B. D. Coral reef origins of atmospheric dimethylsulfide at Heron Island, southern Great Barrier Reef, Australia. *Biogeosciences* **14**, 229 (2017).
254. Spiro, P. A., Jacob, D. J. & Logan, J. A. Global inventory of sulfur emissions with 1×1 resolution. *J. Geophys. Res. Atmos.* **97**, 6023–6036 (1992).
255. Steudler, P. & Peterson, B. Contribution of gaseous sulphur from salt marshes to the global sulphur cycle. *Nature* **311**, 455–457 (1984).
256. Ksionzek, K. B. et al. Dissolved organic sulfur in the ocean: biogeochemistry of a petagram inventory. *Science* **354**, 456–459 (2016).
257. Webb, A. et al. Extreme spikes in DMS flux double estimates of biogenic sulfur export from the Antarctic coastal zone to the atmosphere. *Sci. Rep.* **9**, 2233 (2019).
258. Galí, M. et al. DMS emissions from the Arctic marginal ice zone. *Elem. Sci. Anthr.* https://doi.org/10.1525/elementa.2020.00113 (2021).
259. Gage, D. A. et al. A new route for synthesis of dimethylsulphoniopropionate in marine algae. *Nature* **387**, 891 (1997).
260. James, F., Paquet, L., Sparace, S. A., Gage, D. A. & Hanson, A. D. Evidence implicating dimethylsulfoniopropionaldehyde as an intermediate in dimethylsulfoniopropionate biosynthesis. *Plant Physiol.* **108**, 1439–1448 (1995).
261. Uchida, A., Ooguri, T., Ishida, T., Kitaguchi, H. & Ishida, Y. in *Biological and Environmental Chemistry of DMSP and Related Sulfonium Compounds* 97–107 (Springer, 1996).
262. Bourgis, F. et al. *S*-methylmethionine plays a major role in phloem sulfur transport and is synthesized by a novel type of methyltransferase. *Plant Cell* **11**, 1485–1497 (1999).
263. Kocsis, M. G. et al. Insertional inactivation of the methionine *S*-methyltransferase gene eliminates the *S*-methylmethionine cycle and increases the methylation ratio. *Plant Physiol.* **131**, 1808–1815 (2003).
264. Trottmann, F. et al. Sulfonium acids loaded onto an unusual thiotemplate assembly line construct the cyclopropanol warhead of a *Burkholderia* virulence factor. *Angew. Chem. Int. Ed. Engl.* **59**, 13511–13515 (2020).
265. Howard, E. C. et al. Bacterial taxa that limit sulfur flux from the ocean. *Science* **314**, 649–652 (2006).

Acknowledgements

This work was supported by UK Research and Innovation via the Natural Environment Research Council and the Biotechnology and Biological Sciences Research Council, through the following grants: NE/L004151/1 (Microbial degradation of DMSO in the marine environment), NE/R010382/1 (Is bacterial DMS consumption dependent on methylamines in marine waters?), NE/P012930/1 (A multidisciplinary study of DMSP production and lysis — from enzymes to organisms to process modelling), NE/X001075/1 (Dimethylsulfoniopropionate cycling in terrestrial environments (DMSP InTerrest)), NE/W009277/1 (ConstrAining the Role of sulfur in the Earth System (CARES)) and BB/X005968/1 (Earth's coolest organosulfur molecule: understanding how agriculture can be more cooling to the climate). Support was also provided by the US National Science Foundation through grant 1807163 (Surface exchange of climate-active trace gases in a sea–ice environment during MOSAiC). The authors thank X. Zhu and B. Williams from the University of East Anglia for discussions and input that informed this Review.

Author contributions

F.E.H. initiated writing of the Review and organized the writing processes. All the authors contributed equally to the discussion and writing of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Peer review information *Nature Reviews Earth & Environment* thanks Sonya Fiddes and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.