Dimethylsulfoxonium propionate - a metabolite extending the marine organosulfur cycle

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Abstract: Algae produce massive amounts of dimethylsulfoniopropionate (DMSP) that fuel the organosulfur cycle.[1,2] On a global scale, several petagrams of this zwitterionic sulfur species are produced annually driving fundamental processes and the marine food web.[1] An important DMSP transformation product is dimethylsulfide that can either be emitted to the atmosphere[3,4] or oxidized to dimethylsulfoxide (DMSO) and other products.[5] Herein, we report the discovery of a new, structurally unusual zwitterionic metabolite dimethylsulfoxonium propionate (DMSOP) that is produced by several DMSP-containing microalgae and marine bacteria. Isotope labeling studies demonstrate that DMSOP is produced from DMSP, and is readily transformed to DMSO by marine bacteria. DMSOP was found in nanomolar amounts in field samples and in media from algal cultures, and thus represents a new biogenic source for DMSO in the marine

environment. The estimated annual oceanic production of oxidized sulfur from this novel pathway is in the teragram range, similar to the calculated DMS flux to the atmosphere.[3] This unprecedented sulfoxonium metabolite is therefore a key metabolite of a novel pathway in the marine sulfur cycle. These findings highlight the importance of a hitherto unknown compound in the marine organosulfur cycle.

Main Text:

The marine organosulfur cycle is fueled by small sulfur-containing zwitterionic osmolytes primarily produced by planktonic algae. The main metabolite of this class, dimethylsulfoniopropionate (DMSP), is produced in impressive amounts of 2 Pg ($2x10^9$ tons) sulfur annually.[1] Cellular DMSP serves important physiological functions in marine algae including but not limited to an osmolyte, a cryoprotectant and an antioxidant.[6,7] Enzymatic lysis of DMSP by DMSP lyases in bacteria and algae yields acrylate and dimethylsulfide (DMS).[8] Volatile DMS is the main source of organosulfur to the atmosphere, with an annual flux of ~30 Tg sulfur[3] it is proposed to affect cloud formation and regulate climate.[4] Dissolved DMSP arising from exudation, grazing, viral lysis, and cell mortality serves as substrate for marine microbes.[7,9,10] In surface waters, substantial quantities of dissolved DMSP and DMS can be detected, but often dissolved dimethylsulfoxide (DMSO) concentration exceeds that for these two species.[5,11] DMSO is mainly produced from bacterial and photochemical DMS oxidation,[12] but algal sources may also be important.[13] Common pelagic bacteria use monooxygenases to oxidize DMS to DMSO,[14] a process that may serve as an energy source.[15] Here we report on the identification of the novel zwitterionic metabolite, dimethylsulfoxonium propionate (DMSOP)

that is widely distributed in phytoplankton and also produced by marine bacteria. This metabolite is the substrate of a novel marine pathway for DMSO production (Fig. 1).

Zwitterionic metabolites, such as DMSP, are difficult to quantify directly and much information on their chemistry and ecology is based on indirect methods. We recently developed an analytical method to directly detect zwitterionic metabolites,[16,17] and observed discrepancies between our analytical data and previous determinations of DMSP and DMSO in plankton samples. We undertook an in-depth survey to determine if additional metabolites could explain this observation, and consistently detected a compound with similar polarity to DMSP in all main classes of microalgae (Fig. 2, Table 1). The high resolution electrospray ionization mass spectrum in positive ionization mode of this metabolite at m/z = 151.0426 was consistent with the formula $C_5H_{11}O_3S$ (calculated m/z = 151.0423), and the isotope peak at m/z = 153.0378 (calculated m/z = 153.0380) confirmed the presence of a sulfur atom in the structure. A fragment ion m/z = 79.0210 was detected by tandem mass spectrometry (MS) that was attributed to protonated DMSO and a fragment at m/z = 73.0283 corresponded to protonated acrylic acid (Fig. 2, Extended Data Fig. 1). Based on the mass spectral data, the signal was tentatively assigned as the sulfoxonium species DMSOP. To obtain a reference compound, DMSOP was synthesized by $RuCl_3$/sodium hypochlorite-mediated oxidation of DMSP, and the structure was confirmed by NMR and MS (Fig. 2, Extended Data Fig. 1 and 2). When this authentic standard was added to an algal extract, it co-eluted with the unknown sulfur-containing metabolite unambiguously proving the identity of this highly unusual compound as DMSOP (Fig. 2d). To our knowledge, only one natural product containing the dimethylsulfoxonium moiety, (2-hydroxyethyl) dimethylsulfoxonium chloride, the causative agent for dogger bank itch from the marine bryozoan *Alcyonidium gelatinosum*[18] and the marine sponge *Theonella* aff. *mirabilis*[19] has been

reported to date. Therefore, the highly polar zwitterionic DMSOP represents a metabolite of a nearly unexplored structural family.

The bloom-forming dinoflagellate *Prorocentrum minimum*, the haptophytes *Prymnesium parvum, Isochrysis galbana,* and *Emiliania huxleyi*, the diatom *Skeletonema costatum*, and other screened diatoms and dinoflagellates all produce DMSOP (Table 1 and Extended Data Table 1) at micromolar to millimolar cellular concentrations, corresponding to 0.13 and 1.2 % of DMSP in the algae (Table 1). DMSOP production in axenic cultures of *I. galbana* and *P. parvum* (Table 1, Extended Data Fig. 3) confirms that phytoplankton are an oceanic source of DMSOP. The metabolite is also released into the medium, and concentrations to up to 0.8 ± 0.2 nM were detected in a stationary axenic *P. parvum* culture.

Since marine heterotrophic bacteria biosynthesize DMSP,[20] we investigated the possibility that DMSOP might also be a bacterial metabolite. Indeed, the DMSP producer *Pelagibaca bermudensis* contained DMSOP (0.32 ± 0.049 pmol μg^{-1} protein, n = 3, ca. 0.1 % of DMSP). Thus, as with DMSP, the oxidized sulfoxonium zwitterion has both a eukaryotic and bacterial origin. This underscores its likely universal distribution in oceanic surface waters. Consistent with this supposition, DMSOP was detected at multiple coastal sites in the NE Pacific, NW Atlantic, Arctic and Mediterranean Sea with an average concentration of 0.14 $\pm$ 0.18 nM. At all sampled stations, DMSOP was above the 0.01 nM limit of detection (Extended Data Table 2). On average DMSOP accounted for 0.22% of DMSP in field samples. This value is consistent with but at the lower end of that observed in culture (vide supra). Based on these findings and compared to the annual DMSP production equivalent to 2 Pg sulfur $year^{-1}$, the corresponding estimated DMSOP sulfur flux is in the teragram range.[1] This sulfur flux through DMSOP is in the same order of magnitude as the total DMS flux to the atmosphere (Fig. 1).[3]

We synthesized isotopically labeled DMSOP and DMSP to study the biosynthesis and catabolism of DMSOP in *P. bermudensis* (Fig. 2b). When $^{13}C_2$-DMSP (labeled methyl groups at the sulfur) was added to batch cultures of *P. bermudensis*, high resolution MS analysis revealed the formation of $^{13}C_2$-DMSOP, with incorporation rates of 3.7 ± 0.6% after 18 h (Fig. 3, Extended Data Table 3). Abiotic $^{13}C_2$-DMSP oxidation to $^{13}C_2$-DMSOP was not observed in the medium controls. Likewise, no singly labeled ^{13}C-DMSOP (m/z = 152.0457) was detected above the intensity of the naturally occurring isotope peak, ruling out an initial DMSP demethylation, subsequent oxidation to the sulfoxide and re-methylation (Extended Data Table 3). This makes the enzymatic oxidation of the positively charged sulfur in DMSP by a hitherto unknown enzyme likely. The direct oxidation of DMSP to DMSOP is also consistent with previous suggestions that DMSP is involved in antioxidant processes either as a consequence of the constitutively high cellular DMSP concentrations in marine algae[21] or the up-regulation of cellular DMSP during oxidative stress.[6] Cellular DMSOP concentrations increased nearly 300% in batch cultures of *I. galbana* during the late exponential phase/stationary phase corresponding to increased oxidative stress indicated by a decrease in the photosynthetic efficiency, *Fv/Fm* (Extended Data Fig. 3). DMSP cellular concentrations changed very little during the growth of *I. galbana*. Due to the constitutively high DMSP concentration this finding is consistent with the supposition that DMSP is a de facto antioxidant,[21] resulting in increased oxidative production of DMSOP from DMSP with increasing oxidative stress.

DMSOP is stable in 0.2 μm-filtered seawater at room temperature over several weeks (Extended Data Fig. 4). However, microbial transformations might contribute to its degradation in the ocean. Marine bacterioplankton, such as *Alcaligenes faecalis,* degrade DMSP by demethylation to methylmercaptopropionate[22] or by lyase-mediated cleavage to DMS and acrylate.[9,23] We

tested the capability of common marine bacteria to degrade DMSOP in a similar pathway. After addition of $^{13}C_2$-labeled DMSOP to an *A. faecalis* culture, DMSO with a >99% degree of $^{13}C_2$-labeling was detected after 24 h, indicating that DMSOP was the exclusive source for DMSO production in this bacterium (Extended Data Fig. 5). Quantification of DMSO after reduction to DMS indicated that all tested bacteria (*Sulfitobacter* sp., *Ruegeria pomeroyi*, *Alcaligenes faecalis*, and *Halomonas* sp.) produced DMSO from DMSOP with different efficacies (Fig. 3, Extended Data Fig. 5).[21] By analogy to DMSP lyase-mediated cleavage, abstraction of the DMSOP alpha proton, followed by release of DMSO and acrylate is a plausible mechanism,[24,25] supported by the observed DMSO release upon base treatment of DMSOP that occurs similarly to base-mediated DMS release from DMSP (Extended Data Fig. 4). *A. faecalis*, a bacterium with the well-identified DMSP-lyase DddY and a mutant where this enzyme was knocked out[24,26] both showed similar DMSO production, suggesting that this DMSP lyase was not involved in DMSOP transformation (Extended Data Fig. 5). It has to be verified if other reported DMSP lyases or in fact a specific DMSOP lyase catalyze the transformation.

Our results demonstrate that a hitherto unrecognized ubiquitous zwitterionic metabolite, DMSOP, contributes to the marine DMSO pool and may partly account for DMSO in marine algae.[13] In light of our findings, a functional role of DMSP as an oxygen acceptor is likely and could explain numerous observations of DMSP regulation under oxidative stress. Algal and bacterial DMSOP biosynthesis and its bacterial degradation to DMSO represent a new pathway for DMSO production extending our current paradigm of the marine sulfur cycle beyond the established biotic/photochemical pathways via DMS oxidation.

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Author Contributions: G.P., K.T., B.G. and D.K designed the research. B.G. identified DMSOP signals, performed the synthesis and the initial screening of the metabolite. K.T. performed DMSOP quantification, experiments on the biosynthesis and transformation in algae and bacteria. N.M. did experiments on DMSOP production and transformation in algae and performed several analytical measurements. The *I. galbana* growth experiment and DMSO quantification was performed by L.C.. D.K. was responsible for field sampling and sample work-up. K.T. and N.M. performed the statistical evaluation of the data. G.P. and D.K. were the principal investigators for their respective research teams. K.T. and G.P. wrote the main drafts of

the manuscript. All authors discussed the results and provided feedback and revisions to the manuscript.

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Author Information: Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interest. Correspondence and requests for materials should be addressed to G.P. (Georg.Pohnert@uni-jena.de) or D.K. (djkieber@esf.edu).

Figure legends:

Figure 1: Simplified, revised marine sulfur cycle. Dimethylsulfoxonium propionate (DMSOP) and the transformations labeled with red arrows extend the established marine sulfur cycle. DMSOP is produced in eukaryotic microalgae (green) as well as in bacteria (blue). Bacteria metabolize this compound and thereby contribute to the marine DMSO pool. The established DMSP-based part of the sulfur cycle is indicated with grey arrows. DMSP is formed by marine algae and bacteria. It is then cleaved by algal and bacterial DMSP lyases to DMS and acrylate (not shown). The subsequent biological and photochemical oxidation of DMS to DMSO, sulfate and other products can occur within algae, bacteria, in the seawater, and the atmosphere.

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241

242 **Figure 2**: **Detection and structural elucidation of DMSOP. a**, Chromatographic profile of
243 zwitterionic metabolites from a *Prorocentrum minimum* culture, separated using UHPLC with
244 detection by electrospray mass spectrometry (ESI MS). The total ion current is shown in grey.
245 The metabolites glycine betaine (GBT, cyan), dimethylsulfonioacetate (DMSA, orange), DMSP
246 (black) and gonyol (blue) were assigned according to Gebser et al.[16] The ion trace of
247 dimethylsulfoxonium propionate (DMSOP, red) is shown in a 10-fold magnification. **b**,
248 Synthesis of authentic (labeled) DMSOP. **c**, Tandem mass spectrum of DMSOP with
249 characteristic fragments. **c,** UHPLC profile monitoring m/z = 151 of an extract of *Prymnesium*
250 *parvum* (solid line) and the same extract treated with synthetic DMSOP in roughly equal
251 amounts (dashed line), the experiment was repeated three times with varying concentrations of
252 synthetic DMSOP to confirm co-elution.

253

Figure 3: Biosynthesis and catabolism of DMSOP. Panel **a** shows the high resolution mass spectrum of DMSOP obtained from *P. bermudensis* incubated for 24h with $^{13}C_2$-labeled DMSP (Fig. 2). The peak labelled in red represents $^{13}C_2$-labeled DMSOP, the natural DMSOP isotopes are shown in black (see also Extended Data Table 3). Panels **b** and **c** illustrate the DMSO release (mean ± s.d.) of the bacteria *Sulfitobacter* sp. and *R. pomeroyi* incubated with 1 µM DMSOP. P values directly over bars indicate significant difference from t = 10 min of the same treatment, P values over braces indicate significant difference between treatment and the control without DMSOP addition (n=4 independent biological replicates for 24 h, n=3 for 10 min and 5 h, for statistical details see Methods).

Methods:

Synthesis of dimethylsulfoxonium propionate (DMSOP)

The synthesis of DMSOP was based on Forrester *et al*.[27] and Ayres and Hossain[28]. To a stirred solution of 100 mg 3-dimethylsulfoniopropionate (DMSP) (synthesized according to Chambers[29]) in 0.5 mL deionized water were added 0.24 mL of an aqueous 0.24 M $RuCl_3$ hydrate solution (Roth, Karlsruhe, Germany) at room temperature. A 12% sodium hypochlorite solution (12% Cl, Roth, Karlsruhe, Germany) was added at room temperature to the dark solution dropwise until the color changed to a yellowish green. When the solution turned brown after stirring few minutes more sodium hypochlorite was added. The pH was adjusted to 5-6 with a 1M HCl solution (37%, Roth, Karlsruhe, Germany) during the reaction. When the solution did not embrown further, the water was removed in a rotary evaporator and the resulting white solid

was dissolved at room temperature in a minimum amount of MeOH. Diethylether (Et_2O) was added dropwise until a precipitate formed. After the precipitate settled within 30 min and additional Et_2O was added. This procedure was repeated until no further precipitate formed. The precipitate was filtered off and dried on the filter. Due to salt residues in the product, elemental analysis (EA), based on sulfur content in the final product relative to theoretical sulfur content of pure DMSOP, was used to determine the degree of purity.

^{1}H-NMR (600 MHz, D_2O) δ ppm: 3.21 (2H, t, J = 6.88 Hz, H(C2)), 3.89 (6H, s, H(C4)), 4.33 (2H, t, J = 6.88 Hz, H(C3)); ^{13}C-NMR (200 MHz, D_2O) δ ppm: 25.49 (C2), 38.68 (C4), 48.48(C3), 172.78(C1); Numbering of carbons and HMBC correlations are shown in Extended Data Fig. 2. ESI-MS (positive) *m/z* 151.56 $[M + H]^+$; ESI-MS-MS (parent ion *m/z* 151, collision energy 15 eV): *m/z* 151.56 $[M + H]^+$, 79.30 $[M - C_3H_5O_2 + H]^+$, 73.29 $[C_3H_4O_2 + H]^+$; EA: calculated C 32.2%, H 5.9%, S 17.2% , Cl 19.0%; found C 25.5%, H 4.7%, S 13.4%, Cl 26.7%; degree of purity 77.8%.

Synthesis of $^{13}C_2$-DMSOP was done as described using $^{13}C_2$-DMSP as starting material. This was synthesized using $^{13}C_2$-DMS according to[29].

Cultivation of Phytoplankton

Cultures were obtained from the Provasoli-Guillard National Center for Marine Algae and Microbiota, East Boothbay, Maine, USA (CCMP strains), the Roscoff Culture Collection, Roscoff, France (RCC strains), the UTEX Algae Express, Austin, Texax (UTX strains) , and the Culture Collection of Algae and Protozoa, Oban, Scotland (SCCAP strains). Axenic *Isochrysis galbana* (CCMP 1323) batch cultures were grown in a modified Guillard f/2 medium without silica in 2.8 L Fernbach flasks. The modified f/2-Si medium consisted of 1 L of autoclaved 0.2

299 μm filtered Sargasso Sea water (salinity 34.9 ppt) enriched with 160 μM $NaNO_3$, 10 μM
300 NaH_2PO_4, 1.0 μM Fe, 11.7 μM EDTA, 39.9 nM Cu, 26.0 nM Mo, 76.5 nM Zn, 42.0 nM Co, 910
301 nM Mn, 296 nM Vitamin B_1, 2.05 nM Biotin, and 0.369 nM Vitamin B_{12}.
302 *I. galbana* cultures were grown under batch conditions with cool white fluorescent lighting (92.7
303 μmol photon m^{-2} s^{-1} between 400 and 700 nm) with a 14:10 h day:night cycle in an incubator
304 (model I-36 LLVL, Percival Scientific, Perry, Iowa). The temperature was maintained at 23.0 ±
305 0.1˚C. Daily sampling started at 10:00 local time. Axenicity was periodically determined by
306 DAPI staining followed by epifluorescence microscopy counting.[21]
307 For DMSOP screening, *Skeletonema costatum* RCC75, *Isochrysis galbana*, *Chaetoceros*
308 *compressum* CCMP168, *Chaetoceros didymus* CH5, *Entomoneis* paludosa, *Nitzschia* cf.
309 *pellucida* DCG0303, *Navicula* sp. I15, *Phaeodactylum tricornutum* CCMP2561, SCCAP K-128
310 and UTX646, axenic *Prymnesium parvum* CCAP 946/6, *Stephanopyxis turris*, *Thalassiosira*
311 *pseudonana* CCMP1335, *Thalassiosira rotula* RCC841, RCC776 and CCMP1018, *Thalassiosira*
312 *weissflogii* RCC76 and *Rhodomonas* sp. were cultivated in an artificial seawater medium.[30]
313 *Phaeocystis pouchetii* AJ01, *Amphidinium carterae* SCCAP K-0406 and *Prorocentrum minimum*
314 were cultivated in a f/2 medium.[31] No silicate was added to the medium used to cultivate
315 *Prorocentrum minimum*. *Coscinodiscus wailesii* CCMP2513, *Lingulodinium polyedrum*
316 CCAP1221/2 and *Symbiodinium microadriaticum* CCMP2464 were cultivated in L1 medium;[32]
317 no silicate was added to the *S. microadriaticum* L1 medium. The medium for *Emiliania huxleyi*
318 was prepared according to Spielmeyer *et al*.[33] Cultivation was done from stock cultures by a 20-
319 fold dilution of a cell suspension in tissue culture flasks. Cultures were grown in a 14:10
320 light:dark cycle with light provided by osram biolux lamps (40 μmol m^{-2} s^{-1} between 400 and
321 700 nm) at 12 °C, except for *Phaeocystis pouchetii* which was cultivated at 5 °C. Cultures were

grown to the exponential phase and then divided into four aliquots of equal volume. These aliquots were 20-fold diluted with fresh medium and cultivated again to the exponential phase before being used for quantitative analysis as described below.

For all cultures except for *I. galbana*, cell counts were determined in a Fuchs-Rosenthal hemocytometer using a Leica DM2000 (Heerbrugg, Switzerland) upright microscope with phase contrast. Cell volumes for *P. minimum* and *E. huxlexi* were obtained from reference[16] whereas other cell volumes were calculated according to[34]. Cell counts and cell volumes for *I. galbana* cultures were determined by adding 200 µL of an unfiltered sample to 10 mL of 0.2 µm-filtered electrolyte diluent (1% sodium chloride in 50 mM phosphate buffer, pH 7.4). Samples were analyzed with a Beckman-Coulter Z2 Particle Counter and Size Analyzer (Pasadena, CA, USA) fitted with a 100-µm aperture.

The photosynthetic efficiency of photosystem II (*Fv/Fm*) was determined during the *I. galbana* growth experiment using a Water-PAM pulse-amplitude modulated (PAM) fluorometer (Walz, Effeltrich, Germany). To determine *Fv/Fm*, triplicate 3 mL aliquots of unfiltered culture samples were dark adapted at room temperature for 30 min. The fluorometer was blanked with 0.2-µm filtered Sargasso seawater. After 30 min, a saturating pulse (~3230 µmol m^{-2} s^{-1}, 0.6 s) was applied to each culture sample for a total of six to eight measurements. Sample dilutions were performed as needed with 0.2-µm filtered Sargasso seawater. Gain settings were 2–3 for PM-gain and 1 for out-gain, except for early in the growth curve when the PM-gain was set at 6 and out-gain was set at 5.

Cultivation of Bacteria

344 *Halomonas* sp. HTNK-1, *Alcaligenes faecalis* M3A and the *dddY* knockout mutant of
345 *Alcaligenes faecalis* M3A (obtained from A. Curson, University of East Anglia, UK[20]) were
346 grown in M9 minimal medium (Sigma-Aldrich, Deisenhofen, Germany). *Ruegeria pomeroyi*
347 DSS-3 and *Sulfitobacter* sp. EE-36 were grown in a marine basal medium. The cultures were
348 grown under gentle shaking at 28 °C with addition of 10 mM sodium succinate as the carbon
349 source. For the incubation experiment, experimental cultures were prepared in four replicates for
350 each sampling point from the stock culture by a 20-fold dilution of an aliquot of cell suspension
351 in tissue culture (TC) flasks and grown to exponential phase. *Pelagibaca bermudensis* DSM
352 15984 (Deutsche Sammlung von Mikroorganismen und Zellkulturen, Braunscheig, Germany)
353 was cultivated in Marine Broth medium (Carl Roth GmbH, Karlsruhe, Germany) and grown
354 under gentle shaking at 28 °C.
355
356 **Field samples**
357 Unfiltered seawater samples were collected from the near surface in Niskin bottles attached to a
358 CTD rosette. For each sample, triplicate 15 mL subsamples were collected directly from the
359 Niskin bottle into three precleaned and baked (550 ^{o}C, 8 h) 20 mL glass scintillation vials, each
360 with a green thermoset screwcap containing a Teflon-faced silicone insert. Samples were
361 collected on three oceanographic cruises: the NW Atlantic on the R/V Endeavor, the NE Pacific
362 aboard the R/V Oceanus, and in the Arctic aboard the Canadian research icebreaker CCGS
363 Amundsen. The Mediterranean Sea samples were collected into 250 mL precleaned polyethylene
364 bottles (pre-rinsed with 5% HCl followed by high purity laboratory water) just below the sea
365 surface; one samples was collected offshore just beyond the breaking waves and one sample was

collected nearshore in the wave breaking zone. A map of the sampling locations is shown in Extended Data Table 2.

Each sample vial was microwaved to boiling (ca. 12 s) with the cap loose. Once the sample cooled to room temperature, it was bubbled with ultra-high purity He (99.9995 %) for 10 min to quantitatively remove DMS (verified by testing for residual DMS by re-sparging the same sample), and then 150 μL of Ultrex concentrated HCl (Baker) was added to each sample to preserve DMSP and DMSOP in their protonated forms followed by storage in the dark at room temperature until analysis.

For chlorophyll *a* samples, from 5 to 50 mL of unfiltered seawater was filtered with a low vacuum (ca. 130 mbar) through a pre-baked (550 ^{o}C, 8 h) GF/C filter (Whatman), and the folded filter placed into a 10 mL borosilicate test tube that was stored at -20 ^{o}C until analysis. Unless otherwise noted, triplicate samples were filtered. Chlorophyll *a* samples were analyzed by adding 5 mL of 90% acetone (10% water) to each test tube. Samples were vortexed and then allowed to incubate overnight at -20 ^{o}C. The chlorophyll fluorescence was then measured with a TD-700 fluorometer.[35]

Extraction and sample preparation for phytoplankton cellular DMSOP

For all cultures except *I. galbana*, to screen for the presence of particulate DMSOP, algal cultures were filtered under reduced pressure (GF/C grade microfiber filter; GE healthcare; Munich) at 400 mbar. Particulate DMSOP in *I. galbana* samples were collected by small volume gravity filtration[36] The filters were immediately transferred to 4 mL glass vials containing 1 mL of methanol and vortexed. Extracts were stored at -20 °C. To prepare a sample for liquid chromatography / mass spectrometry (LC/MS) analysis, 50 μL of the extract was diluted with

100 µL of a mixture of acetonitrile and water (9:1 *v/v*). For ultra performance liquid chromatography / mass spectrometry (UPLC/MS) analysis, 10 µL of an aqueous solution of the internal standard D_6-dimethylsulfonioacetate (D_6-DMSA) was added to the extract prior to injection. The D_6-DMSA was synthesized according to Howard and Russel[37] and Gebser and Pohnert.[16] After centrifugation (5 min, 4,500 rcf) the supernatant was submitted to LC/MS analysis.

Extraction and sample preparation for dissolved DMSOP

To quantify dissolved DMSOP, a dense *P. parvum* culture was divided into four aliquots of equal volume and 20-fold diluted with fresh medium. On day 1, 5, 7 and 11, 1 mL of culture was centrifuged in an Eppendorf tube for 5 min at 100 rcf. The supernatant was transferred to a 1.5 mL glass vial and 5 µL was directly submitted to Ultra high pressure liquid chromatography/high resolution mass spectrometry (UHPLC/HRMS) for analysis.

Extraction and sample preparation for bacterial DMSOP

Aliquots of the bacterial cultures (100 µL) were centrifuged for 5 min at 16,100 rcf, and the supernatant was removed by pipetting. The pellets were taken up in 100 µL of a mixture of acetonitrile and water (9:1 *v/v*) and samples were frozen at -20°C and stored overnight. After thawing the samples, cells were disrupted by sonication using ten pulses in a Bandelin sonoplus ultrasound homogenizer (Bandelin, Berlin, Germany). The samples were again centrifuged for 5 min at 16,100 rcf and 5 µL of the supernatant was directly submitted to UHPLC/HRMS for analysis.

412 **Extraction and sample preparation for field samples**

413 For determination of DMSOP in field samples, 3 mL of the respective sample was freeze dried
414 and re-dissolved in 500 µL acetonitrile. Due to the high salt content of the sample a precipitate
415 remained that settled. The supernatant was transferred to a 1.5 mL glass vial and the samples
416 were dried in a gentle nitrogen stream at 30 °C and resolved in 300 µL of a mixture of
417 acetonitrile and water (9:1 *v*/*v*). After centrifugation (5 min, 4,500 rcf), the supernatant was
418 stored at -80 °C until UPLC/MS measurement.

419

420 **UPLC/MS analysis**

421 Analytical separation and quantification of DMSOP in the algal extracts for results shown in Fig.
422 2, Table 1 and Extended Data Table 1 were performed using an Acquity UPLC (Waters, Milford,
423 MA, USA) equipped with a SeQuant ZIC®-HILIC column (5 µm, 2.1 × 150 mm, SeQuant,
424 Umeå, Sweden). Quantification followed a previously reported protocol with modifications as
425 follows:[38] The eluent consisted of high purity water with 2% acetonitrile and 0.1% formic acid
426 (solvent A) and 90% acetonitrile with 10% 5 mmol L^{-1} aqueous ammonium acetate (solvent B).
427 The flow rate was set to 0.60 mL min^{-1}. A linear gradient was used for separation with 100%
428 solvent B (1 min), 20% B (6.5 min), 100% B (7.1 min), 100% B (10 min). The column was kept
429 at 25 °C. A Q-ToF micro mass spectrometer (Waters Micromass, Manchester, England) with
430 electrospray ionization in positive mode was used as the mass analyzer. The sample cone was set
431 to 18 V, the extraction cone to 1 V, the sheath gas was operated at 20 L h^{-1} and the desolvation
432 gas at 450 L h^{-1}. MS/MS for fragmentation of DMSOP was accomplished with a collision energy
433 of 15 eV. Calibration curve: area [DMSOP] = 123 * c [DMSOP in µM] with r = 0.9983, LOD =
434 0.05 µM LOQ = 0.1 µM. Data analyses were done using the software MassLynx 4.1.

435

436 **UHPLC/HRMS analysis**

437 All other LC/MS results were obtained on a Dionex Ultimate 3000 system (Thermo Scientific™,
438 Germering, Germany) coupled to an Exactive™ Plus Orbitrap mass spectrometer (Thermo
439 Scientific™, Bremen, Germany). Electrospray ionization was performed in positive mode
440 ionization with the following parameters: capillary temperature 380 °C, spray voltage 3000 V,
441 sheath gas flow 60 arbitrary units and aux gas flow 20 arbitrary units. The LC separation column
442 and the solvent gradient were identical to that described in the previous section on UPLC/MS
443 analysis; the injection volume was 5 µL.
444 Calibration curves for DMSP and DMSOP were recorded in triplicate using synthetic standards
445 prepared as described above and in reference[29]. For DMSOP, the LOD was 0.01 nM, the LOQ
446 0.1 nM and the linear range between 0.1 and 1000 nM. Calibration curve: area [DMSOP] =
447 418370 * c [DMSOP in nM] with r = 0.9998. For DMSP, the calibration curve was: area
448 [DMSP] = 470540 * c [DMSP in nM] with r = 0.9999. MS/MS for fragmentation of DMSOP
449 was accomplished with a normalized collision energy of 35. Data analyses were done using the
450 software Thermo Xcalibur version 3.0.63.

451

452 **DMSO quantification using purge and trap GC/FPD**

453 Analyses of samples to quantify DMSO were done according to[21]. Briefly, 3 mL of unfiltered
454 culture samples were pipetted into 4 mL glass vials (see method section **DMSOP**
455 **Transformation** for details) and stored frozen until analysis. For analysis, samples were first
456 tested to see if they contained DMS. Since no DMS was detected in the samples, they were not
457 bubbled with UHP He to remove the DMS prior to analysis. The total DMSO in unfiltered

458 culture samples or medium controls was measured after reduction to DMS by $TiCl_3$.[21] For each
459 sample, a 1 mL aliquot was amended with 200 µL $TiCl_3$ reagent (20% w/v in 2 M HCl, EMD
460 Chemicals) in a 14 mL serum vial that was crimp sealed with a Teflon-lined butyl rubber stopper
461 and an aluminum crimp cap. The DMSO samples were reacted for 1 h at 55 ˚C, then cooled to
462 room temperature for analysis.
463 Reacted vials containing DMS were sparged with UHP He for 3 min to transfer the DMS from
464 the vials onto liquid-nitrogen cooled Teflon wool using a custom-made cryogenic purge-and-trap
465 system. Hot water (ca. 90 ^{o}C) was used to desorb the DMS from the Teflon wool and inject the
466 sample into Shimadzu GC-14A gas chromatograph equipped with a Chromosil 330 column (2.4
467 m Long × 3.2 mm i.d., Supelco Inc.). The sulfur was detected with a sulfur-selective flame
468 photometric detector. The column temperature was set isothermally at 60 ˚C. Both the injection
469 port and detector temperature were set at 225 ˚C. Authentic DMSP and DMSO standards were
470 prepared in the same manner as the samples. The LOD of the method is 0.2 pmol S for a 1 mL
471 aqueous sparged sample, with a signal-to-noise ratio of two.
472
473 **Confirmation of DMSOP in the algal extract**
474 A *Prymnesium parvum* methanolic extract from a stationary growth-phase culture was used to
475 determine if the signal of the unknown metabolite in the extract co-eluted with an authentic
476 DMSOP standard that was added to the extract prior to injection into the UPLC. As a control,
477 50 µL of the extract with no DMSOP standard was diluted with 100 µL of a mixture of
478 acetonitrile and water (9:1, *v*/*v*). After centrifugation (5 min, 4,500 rcf), the supernatant was
479 injected into the UPLC. In a separate analysis, an aliquot of this *P. parvum* extract was amended
480 with 10 µL of a 10 µM DMSOP standard solution, and then prepared for analysis in the same

481 way as the control. Comparison of the peaks of mass trace $m/z = 151$ for the two injections
482 showed an increased area at a retention time of $t_R = 4.2$ min corresponding to the DMSOP-
483 amended extract.
484
485 **DMSP transformation**
486 *P. bermudensis* cultures (6.5 mL, OD = 1.97 ± 0.05, protein content = 99 ± 1.3 µg mL^{-1}, n = 3)
487 were concentrated by centrifugation to 1 mL before addition of 10 µL of $^{13}C_2$-DMSP (10 mM in
488 H_2O). Samples were maintained under shaking at 28 °C for 18 h. Aliquots (100 µL) of the
489 cultures were centrifuged and the pellet was treated as previously described for DMSOP
490 quantification.
491
492 **DMSOP transformation**
493 Prior to incubation, aliquots of the bacterial cultures (10-15 mL) were washed three times by
494 centrifugation (15 min, 4,500 rcf) and subsequently resuspended in 10 mL of a succinate-free
495 medium to remove excess of organic carbon. For incubation experiments, all bacterial cultures
496 were diluted with succinate-free medium to an optical density of OD = 0.10-0.12. Culture
497 samples (3 mL each) were transferred into 4 mL screw cap vials with PTFE/silicone septa, each
498 vial containing a glass-coated stirrer. After addition of either an aqueous DMSOP solution (0.65
499 mM) with a final concentration of 1 µM or the same amount of water (controls), the vials were
500 sealed, vortexed and placed on a shaker at 28 °C. Samples and controls were prepared for each
501 culture in four replicates. Samples were taken directly after substrate addition (10 min), and after
502 5 and 24 h. The vials were frozen at -20 °C until DMSO quantification. As controls, MBM and

503 M9 medium with added DMSOP at a final concentration of 1 µM were prepared in four
504 replicates. Incubation conditions and sampling times were done as described above.
505
506 **GC/HRMS measurement of $^{13}C_2$-DMSO**
507 To determine if DMSOP was a DMSO precursor, we developed a method for the determination
508 of DMSO using solid phase microextraction in combination with gas chromatography/HRMS.
509 DMSO was extracted as described above for DMSOP transformation in 4 mL glass vials sealed
510 with PTFE septa. Extraction was achieved with a solid phase microextraction (SPME) fiber
511 (100 µm PDMS, Supelco, Deisenhofen, Germany). Prior to extraction, the SPME fiber was
512 conditioned for 15 min at 250 °C. To apply the fiber to the sample vial, a hole was pierced in the
513 septum and the needle of the SPME holder was inserted into the vial. By immersion of the fiber
514 into the constantly stirred solution the analyte was allowed to adsorb onto the fiber for 15 min at
515 room temperature. Subsequently, the fiber was inserted into the injection port of the GC. DMSO
516 was desorbed into the PTV injector at 300 °C for 5 min in a gas chromatograph (TRACE™
517 1310, Thermo Scientific) that was fitted with a 60 m x 0.25 mm 1 µm film ZB-1MS capillary
518 column (Phenomenex, USA) and a hybrid quadrupole-orbitrap mass spectrometer (Q Exactive,
519 Thermo Scientific). Ultrahigh purity helium was used as carrier gas at a flow of 1.2 mL min^{-1}.
520 The oven temperature was held for 1 min at 40 °C and subsequently increased to 150 °C (15 °C
521 min^{-1}) and again held for 3.5 min. The transfer line and ion source were both set to 300 °C. Mass
522 measurements were performed in EI-positive mode. A mass range from 45 to 200 *m*/*z* was
523 recorded. The ionization energy was 70 eV and scan time 0.25 s. Data analyses were performed
524 with the Thermo Xcalibur software version 3.0.63.
525

DMSOP base lability

2.5 µL of a 0.5 M NaOH solution was added to 1 mL of an aqueous DMSOP solution in water (500 µM). A DMSOP solution without addition of NaOH served as a control. Samples were prepared in triplicate. To determine DMSO, samples (50 µL) were taken immediately after the addition of NaOH (0 min), and after a reaction time of 2.5, 5.3 and 23 h at room temperature. DMSO was detected by UHPLC/HRMS using a Rezex ROA-Organic Acid (8%) column (8 µm, 4.6 × 150 mm, Phenomenex, USA). Separations were carried out isocratically at 90% 0.0025 M trifluoroacetic acid (solvent A) and 10% acetonitrile (solvent B) for 12 min. The flow rate was set to 0.40 mL/min. DMSOP was quantified as described above.

Statistical analysis

Data is given as mean ±s.d., the number of replicates n is listed. For comparison of two groups an unpaired two-tailed t-test was used. As prerequisites normal distribution (Shapiro-Wilk) and equal variance were tested. If at least one of those prerequisites was not met ($P \geq 0.05$) a Mann-Whitney Rank Sum Test was performed. For comparison of multiple time points a One Way ANOVA was utilized. If prerequisites were not met a Kruskal-Wallis One Way ANOVA on Ranks was performed. If samples were drawn repeatedly from the same vessel a One Way Repeated Measurement ANOVA was used. All ANOVA were followed by a Tukey post hoc test for multiple pairwise comparisons if there was a significant difference in the dataset. All statistical analyses were performed with a 95% confidence interval using Sigma-Plot version 11.0. $P > 0.05$ is considered not significantly different. For results in Fig. 3b no equal variance was observed within the treatment "control" and Kruskal-Wallis One Way ANOVA on Ranks with Tukey post hoc test for different time points was conducted. Within the treatment

549 "+DMSOP" a One Way ANOVA with Tukey post hoc test for different time points was
550 conducted. Within time points (10 min and 24 h) unpaired two-tailed t-tests between "control"
551 and "+DMSOP" were performed. Within time point (5 h) a normal distribution was not observed
552 and therefore a Mann-Whitney Rank Sum Test was conducted to compare between control and
553 treatment. For results in Fig. 3c a One Way ANOVA with Tukey post hoc test for different time
554 points was conducted within the treatment "control" and within the treatment "+DMSOP".
555 Within time points (10 min and 5 h) unpaired two-tailed t-test between "control" and
556 "+DMSOP" were conductedFor the 24h time point no equal variance was given and a Mann-
557 Whitney Rank Sum Test was performed. The loss of a medium control sample during transport
558 led to the exclusion of one replicate of the treatment "+DMSOP" (t = 10 min) from the analysis
559 in Fig. 3b and c. A contaminated medium control sample led to exclusion of a replicate of the
560 treatment "+DMSOP" (t = 5 h) from the analysis in Fig 3b and c.

561

562 **Data availability:** The datasets generated and analyzed during the current study are available
563 from the corresponding authors on reasonable request.

564

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Extended Data

Extended Data Figure 1: DMSOP mass spectra. The HR MS/MS spectra of natural occurring DMSOP and the authentic standard (normalized collision energy of 35) are shown. **a,** DMSOP standard, molecular ion *m*/*z* 151.0421, fragments $[C_2H_7O_2S]^+$ *m*/*z* 79.0210 and $[C_3H_5O_2]^+$ *m*/*z* 73.0283. **b**, Isotopic pattern of the molecular ion *m*/*z* 151.0421 with the calculated formula $C_5H_{11}O_3S$ and isotopic fine structure of [M+1] and [M+2]. **c,** DMSOP from a *P. parvum* extract with added $^{13}C_2$-DMSOP. **d**, $^{13}C_2$-DMSOP, molecular ion *m*/*z* 153.0485, fragments $[^{13}C_2H_7O_2S]^+$ *m*/*z* 81.0277 and $[C_3H_5O_2]^+$ *m*/*z* 73.0282.

Extended Data Figure 2: Structure of DMSOP. Arrows show the heteronuclear multiple bond coherence (HMBC) correlations. Numbers indicate carbon atom positions.

Extended Data Figure 3: *I. galbana* growth and cellular DMSOP. Growth (**a**) and photosynthetic efficiency (**b**) of *I. galbana* cultures. Cellular DMSP and DMSOP content are given in **c**. Data represent mean values of n=3 independent cultures ± s.d.. P values are from One Way Repeated Measurement ANOVA with Tukey post hoc test. A significant difference in cellular DMSOP concentration compared to day 3 is detected from day 7 onward.

Extended Data Figure 4: DMSOP is stable in seawater but base labile. DMSOP is stable over a period of 72 days in seawater (**a** left). It degrades at room temperature under basic pH (pH

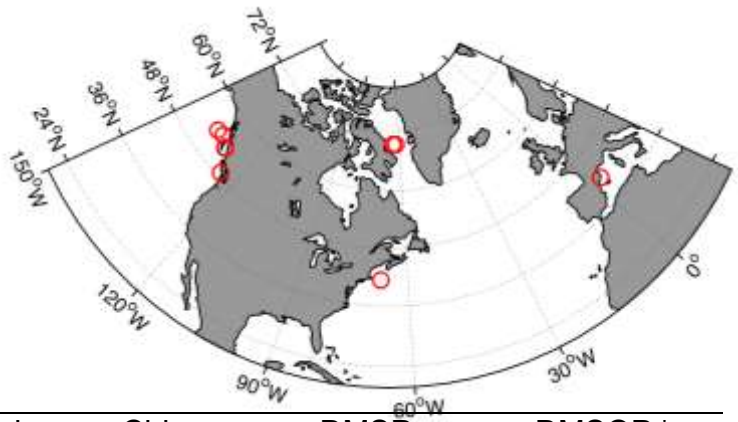
623 = 11, monitored over 23 h, **a** right). DMSO is released during this base treatment (integration of
624 *m*/*z* = 79 in GC/MS, **b**). Mean values are given and error bars denote the s.d. for the independent
625 analysis of n=3 separate cultures. P values are from One Way Repeated Measurement ANOVA
626 with Tukey post hoc test compared to t = 0 h.

627 **Extended Data Figure 5: DMSO release from DMSOP by bacteria.** DMSOP (1 μM) is
628 degraded by *A. faecalis*, a *dddY* knock out mutant of *A. faecalis* (**a**) and by *Halomonas* sp. (**b**).
629 Data represent mean values of n=4 independent cultures ± s.d.. P values result from unpaired
630 two-tailed t-tests. In separate experiments (**c**) it was demonstrated that DMSOP is the exclusive
631 source for DMSO production in *A. faecalis*. Release of labeled DMSO from $^{13}C_2$-DMSOP was
632 monitored by HR-GC/MS. The mass spectrum shows an average over the DMSO peak extracted
633 from an *A. faecalis* culture that was incubated for 23 h with DMSOP. Integration of the ion
634 traces 80.0200 ($^{13}C_2$-DMSO) and 78.0134 (DMSO) in three independent replicates revealed a
635 degree of labeling of 99.3 ± 0.25%.

Extended Data Table 1: Occurrence of DMSOP in different algal species. (+) DMSOP above the limit of detection of 0.08 µM (UPLC/MS analysis), (-) DMSOP below the limit of detection. The ratio of peak area (DMSOP)/peak area (DMSP) was > 0.01% in all samples labeled with (+). Cultures without strain denomination are from our culture stock in the laboratory of the Institute of Inorganic and Analytical Chemistry Jena (strains available upon request).

Class	Species	Strain	DMSOP
haptophyte	*Isochrysis galbana*		+
	Prymnesium parvum (axenic)		+
	Prymnesium parvum	CCAP946/6	+
	Phaeocystis pouchetii	AJ01	-
diatom	*Chaetoceros compressum*	CCMP168	-
	Chaetoceros didymus	CH5	-
	Coscinodiscus wailesii	CCMP2513	+
	Entomoneis paludosa		+
	Eucampia zodiacus		+
	Nitzschia cf. *pellucida*	DCG0303	-
	Navicula sp.	I15	-
	Phaeodactylum tricornutum	CCMP2561 SCCAP K-128 UTX646	-
	Skeletonema costatum	RCC75	+
	Stephanopyxis turris		-
	Thalassiosira pseudonana	CCMP1335	-
	Thalassiosira rotula	RCC841 RCC776 CCMP1018	-
	Thalassiosira weissflogii	RCC76	-
coccolithophore	*Emiliania huxleyi*	RCC1217 RCC1731	+
cryptophyceae	*Rhodomonas* sp.		-
dinoflagellate	*Amphidiniuim carterae*	SCCAP K-0406	-
	Lingulodinium polyedrum	CCAP1121/2	-
	Prorocentrum minimum		+
	Symbiodinium microadriaticum	CCMP2464	+

Extended Table 2. Map of sampling sites and $DMSP_{total}$ and $DMSOP_{total}$ concentrations in seawater. The error is the standard deviation (n=3 independent samples). When no s.d. is reported n = 1.



* Limit of quantification of 0.1 nM, limit of detection = 0.01 nM (UHPLC/HRMS analysis)

Location	Date (2016)	Latitude (˚N)	Longitude (˚W)	Depth (m)	Temp. (°C)	Sal. (ppt)	Chl *a* (μg L^{-1})	$DMSP_t$ (nM)	$DMSOP_t$* (nM)
NW Atlantic	Sept 21	41.40	67.47	5	18.5	32.5	3.14 ± 0.02	16.7 ± 1.4	0.057 ± 0.048†
Arctic	July 9	69.50	61.58	10	-0.7	32.8	0.47	44.8 ± 2.4	0.197 ± 0.257
	July 10	69.50	63.23	12	-1.3	32.3	0.24	37.8 ± 2.4	0.057 ± 0.043
NE Pacific	July 14	54.04	137.16	5	13.6	32.1	0.63 ± 0.01	49.3 ± 6.9	0.061 ± 0.037
	July 15	54.30	134.68	5	14.9	31.8	0.55 ± 0.01	34.1 ± 1.6	0.036 ± 0.003
	July 19	52.90	130.62	5	13.1	31.5	6.09 ± 0.12	83.1 ± 7.9	0.151 ± 0.015
	July 19	52.96	130.73	5	14.2	31.5	1.80 ± 0.01	49.7 ± 3.0	0.190 ± 0.081
	July 22	48.75	125.42	5	14.9	31.0	16.5 ± 0.57	122.0 ± 15.5	0.079 ± 0.021
Mediterranean	July 18	41.55	2.49‡	surface	24.5	37.4	1.21	24.8 ± 4.5	0.073 ± 0.050
Sea	July 18	41.55	2.49‡	surface	24.5	37.4	1.04	60.5 ± 6.3	0.045 ± 0.037

† n = 2. Range reported.

‡ °E

654 **Extended Data Table 3. Incorporation rates of $^{13}C_2$-DMSP into DMSOP in *P. bermudensis***

655

Peak area $^{13}C_2$-DMSOP *m/z* 153.0496	**Peak area $^{13}C_1$-DMSOP*** *m/z* 152.0455	**Peak area DMSOP** *m/z* 151.0423	**Degree of labeling [%]** $^{13}C_2$-DMSOP in relation to DMSOP†
3,140,000 ± 640,000	4,310,000 ± 180,000	84,700,000 ± 4,080,000	3,68 ± 0,59

656 * The area corresponds to ca 5.1% of the unlabeled isotopologue, which is in accordance with the natural ^{13}C-content of a compound
657 with five carbon atoms (5.5 %). †Values exceed the calculated degree of labeling of the natural isotopologue of 0.26 % and confirm
658 that externally added labeled DMSP was transformed to DMSOP. Data represent mean values of n=3 independent experiments ± s.d..

659