The role of differential DMSP production and community composition in predicting variability of global surface DMSP concentrations

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Abstract

Dimethylsulfoniopropionate (DMSP) is an important labile component of the marine dissolved organic matter pool that is produced by the majority of eukaryotic marine phytoplankton and by many prokaryotes. Despite decades of research, the contribution of different environmental drivers of DMSP production to regional and seasonal variability remains unknown. A synthesis of the current state-of-knowledge suggested that approximately half of confirmed DMSP producers are low producers (intracellular DMSP < 50 mM). Low DMSP producers (LoDPs; e.g., diatoms) were shown to strongly regulate intracellular DMSP concentrations (~16-fold change) as a predictable function of nutrient stress. By comparison, high DMSP producers (HiDPs; e.g., coccolithophores) showed very little response (~1.5-fold change). To assess the importance of differential DMSP production by low and high producers, DMSP concentrations were predicted for two time-series sites (a high- and low-productivity site) and for the global ocean by explicitly incorporating both community composition and mechanistic nutrient stress. Despite large, predictable intracellular DMSP changes, low producers contributed less than 5% to global DMSP. This indicates that, while variations in DMSP production by low producers could be important for predicting microbial interactions and low producer physiology, it is not necessary for predicting global DMSP concentrations. Our analysis suggests that community composition, particularly HiDP biomass, is the dominant driver of variability in in situ DMSP concentrations, even in low-productivity regions where high producers are typically the subdominant group. Accurate predictions of in situ DMSP concentrations require improved representation of subdominant community dynamics in ecosystem models and remote-sensing algorithms.

The marine dissolved organic matter (DOM) reservoir stores an equivalent amount of carbon as the atmosphere and fuels microbial life in the upper ocean (Moran et al. 2016). The labile fraction of DOM is rapidly turned over in the surface ocean on timescales of minutes to weeks (Carlson and Hansell 2014). This is especially true for compounds containing nitrogen, phosphorus, and sulfur that are preferentially remineralized in the upper ocean to support microbial growth (Bronk et al. 1994; Dyhrman et al. 2007; Ksionzek et al. 2016). Dimethylsulfoniopropionate (DMSP) is one of the few identified compounds comprising the rapidly cycled, labile dissolved organic sulfur pool (Ksionzek et al. 2016). Dissolved DMSP has been shown to turn over multiple times a day and supply up to 13% of the bacterial carbon and up to 100% of the bacterial sulfur demands (Kiene et al. 2000; Tripp et al. 2008; Levine et al. 2015). In addition, one of the by-products of DMSP degradation, dimethylsulfide (DMS), is a climatically active trace gas that serves as an important source of cloud condensation nuclei in the remote marine boundary layer (Charlson et al. 1987; Quinn et al. 2017) and significantly contributes to Earth’s radiative budget (e.g., Thomas et al. 2010). Both DMS and DMSP have been shown to act as important infochemicals in microbial interactions at the microscale (Seymour et al. 2010; Johnson et al. 2016). Yet, the mechanisms driving cellular DMSP regulation and variations in in situ particulate DMSP (DMSPp) concentrations are still not fully understood.

A seminal work by Keller et al. (1989) provided the first analysis of the diversity of DMSP producers by surveying 123 marine phytoplankton cultures from the Center for Culture of Marine Phytoplankton (CCMP, now the National Center for Marine Algae) grown under nutrient-replete conditions. Based on this study, phytoplankton have conventionally been divided into two functional groups: high DMSP producers (HiDPs) with intracellular concentrations > 100 mM DMSP and low DMSP producers (LoDPs) with intracellular...
concentrations < 50 mM DMSP. In the proceeding decades, many hypotheses for the physiological function of DMSP have been proposed, including an osmolyte, a cryoprotectant, a ballasting mechanism, a signaling molecule, an overflow mechanism, and an antioxidant (Karsten et al. 1996; Stefels and Van Leeuwe 1998; Stefels et al. 2000; Sunda et al. 2002; Seymour et al. 2010; Lavoie et al. 2015). A unifying aspect of these hypotheses is that all mechanisms propose that DMSP synthesis will be upregulated under different types of cellular stresses (e.g., changes in osmotic pressure or increases in reactive oxygen species production). More than 50 studies have quantified the effect of a wide array of environmental stressors on DMSP production using phytoplankton monocultures (e.g., nitrate limitation, low pH, and UV stress). However, these studies often show conflicting results (e.g., van Rijssel and Gieskes 2002; Archer et al. 2010) suggesting that DMSP may play multiple roles in the cell or different roles for different phytoplankton species (Archer et al. 2010; Bucciarelli et al. 2013). Exactly what those different roles are and how they vary by functional group (e.g., HiDPs vs. LoDPs) remains unclear. In a review article, Stefels et al. (2007) hypothesized that HiDPs may not significantly change cellular DMSP concentrations in response to nutrient stress, while LoDPs appeared to respond with large changes in cellular DMSP. However, to date, there has not been a synthesis of the published literature to test this hypothesis.

In situ DMSPp concentrations are a function of both the abundance of DMSP producers and changes in cellular DMSP in response to environmental conditions. Previous work has primarily focused on HiDPs, particularly Phaeocystis and Emiliania huxleyi, based on the assumption that HiDPs will dominate DMSP production due to high-intracellular concentrations (Stefels 2000). This relationship appears to hold true for highly productive regions with classic spring blooms (e.g., North Atlantic and Southern Ocean) where several previous studies have observed a significant relationship between in situ DMSPp and HiDP biomass (Turner et al. 1988; Malin et al. 1993; Scarratt et al. 2002; Speeckaert et al. 2018). However, seasonal changes in DMSPp concentrations in low productivity, oligotrophic regions have been more difficult to predict (e.g., Masotti et al. 2016). The assumption that DMSPp production by LoDPs is not environmentally relevant is based on intracellular quotas measured in replete laboratory (i.e., nonstressed) conditions (Keller et al. 1989). More recent studies have shown that, under environmental stress (e.g., iron limitation), LoDPs significantly upregulate intracellular DMSP to concentrations that approach those of HiDPs (e.g., Bucciarelli et al. 2013). This suggests that LoDPs, which include many important primary producers such as diatoms and cyanobacteria, may contribute significantly to DMSPp cycling, particularly in oligotrophic regions where environmental stress is highest (Behrenfeld et al. 1993, 2005).

Both numerical ecosystem models and remote-sensing algorithms have been used previously to estimate in situ DMSPp. Prognostic ecosystem models that incorporate DMSP modules (e.g., Belviso et al. 2012) predict in situ DMSPp using literature values of DMSP : carbon ratios for a small number of phytoplankton types. These models tend to both underestimate DMSPp in the oligotrophic oceans and struggle to capture observed seasonal dynamics (e.g., Vogt et al. 2010). A remote-sensing-based estimate of in situ total DMSP (DMSPt) successfully reproduced global DMSPt patterns over a wide range of biomass, but required two different fits to represent mixed and stratified regimes, which implicitly incorporate differences in light and nutrient status (Gali et al. 2015). Validation of DMSP predictions is difficult, particularly for low-biomass regions, as measurements of in situ DMSP are greatly biased toward higher biomass regions: in the PMEL DMS database (Kettle et al. 1999; Lana et al. 2012), there are ~100 DMSPt data points reported between 20°N and 30°N compared to >1300 data points reported between 50°N and 60°N (Gali et al. 2015, 2018).

To provide mechanistic insight into the drivers of variability in DMSPp concentrations, we identified over-arching trends in the regulation of intracellular DMSP in response to nutrient stress using previously published monoculture physiology studies supplemented with new measurements. Here, we focused on nutrient stress responses as the current body of literature does not allow for comparison of HiDP and LoDP DMSP regulation under other stressors. The experimentally derived equations parameterizing the relationship between intracellular DMSP of LoDPs and HiDPs and nutrient stress were then used to mechanistically predict DMSPp as a function of both community composition and environmental stress at two time-series sites and globally using a biogeochemical ecosystem model. LoDPs were shown to strongly upregulate intracellular DMSP as a predictable function of growth limitation due to nutrient stress, while HiDPs exhibited a seemingly constitutive production of DMSP. We show that the magnitude of change in intracellular DMSP due to nutrient stress plays a minor role in determining in situ DMSPp, and that community composition, particularly HiDP biomass, is the driving mechanism of variability in seasonal and regional differences of in situ DMSPp.

Methods

Diversity of DMSP producers

The known diversity of DMSP producers was assessed using previously published studies that confirmed DMSP production (Supporting Information Table S1). These studies used indirect measurements of DMSP through derivatization to DMS and gas chromatography (GC) detection. We only included measurements from monoculture studies as in situ estimates of species specific DMSP concentrations (e.g., Archer et al. 2011) could be biased by the uptake of dissolved DMSP which can vary significantly by species (Vila-Costa et al. 2006; Lavoie et al. 2018).

We supplemented the published data by quantifying DMSP in monocultures of 20 additional phytoplankton strains, including: cyanobacteria (Crocosphaera watsonii [WH003], Crocosphaera
Intracellular DMSP regulation as a function of nutrient stress

All known previous studies that report the effect of nutrient limitation (CO₂, N, Fe, P, Si, or stationary/senescence phase) on cellular DMSP were assessed. For each study, DMSP values were extracted from the text as reported by the authors. If values were not reported in the text, data was extracted from figures using the MathWorks GRABIT GUI program. To allow for intercomparison, only studies reporting intracellular DMSP concentrations in mmol DMS cell L⁻¹ (mM) were included in the analysis (n = 11) (Supporting Information Table S2).

For each study, a fold change due to environmental stress was calculated as:

\[ FC_{q,k} = \frac{\text{DMSP stressed}_{q,k}}{\text{DMSP replete}_{q,k}} \]  

where \( FC_{q,k} \) is the fold change for phytoplankton strain \( q \) under nutrient limitation \( k \). DMSP stressed\(_{q,k} \) is intracellular DMSP measured under nutrient limitation, and DMSP replete\(_{q,k} \) is intracellular DMSP measured under nutrient replete (nonstressed) conditions. For the majority of studies, intracellular DMSP concentrations were quantified during mid-exponential growth under replete (DMSP replete\(_{q,k} \)) and nutrient-limited (DMSP stressed\(_{q,k} \)) conditions. If intracellular DMSP was measured across a batch growth curve (e.g., Franklin et al. 2010), the observed value from the late exponential or stationary phase was used for DMSP stressed\(_{q,k} \) and the observed value from mid-exponential growth was used for DMSP replete\(_{q,k} \).

For each \( FC_{q,k} \) the impact of nutrient limitation on growth was calculated as:

\[ \gamma_{q,k} = \frac{\mu_{q,k}}{\mu_{\text{max}}_{q,k}} \]  

where \( \gamma_{q,k} \) is growth limitation for phytoplankton strain \( q \) due to nutrient stress \( k \), \( \mu_{q,k} \) is the reported growth rate under nutrient limitation, \( \mu_{\text{max}}_{q,k} \) is the reported growth rate under nutrient replete conditions. \( \gamma_{q,k} \) ranges from 1 (unstressed) to 0 (completely inhibited).

The relationship between intracellular DMSP and growth limitation was derived for each study. For LoDPs, there were a total of 11 fits (Thalassiosira pseudonana \( [n = 7] \), Thalassiosira oceanica \( [n = 2] \), Skeletonema marinoi \( [n = 1] \), Trichodesmium erythraeum \( [n = 1] \)) (Supporting Information Fig. S1). When LoDP intracellular DMSP was measured for three or more significantly different growth rates \( (n = 5) \), a sigmoidal function was fit to the data:

\[ I_{q,k} = p1_q + \frac{p2_q - p1_q}{1 + e^{(p3_q - \gamma_{q,k})/p4_q}} \]  

where \( I_{q,k} \) is intracellular DMSP (mM), \( \gamma_{q,k} \) is growth limitation, and \( p1_q, p2_q, p3_q, p4_q \) are best fit parameter values for phytoplankton strain \( q \) determined using a Levenberg-Marquardt nonlinear regression. This form was chosen as it best approximated the observed response curves with \( R^2 > 0.9 \) for the parameter fits.
If only two significantly different growth rates were reported for LoDPs ($n = 6$), a linear fit was used:

$$I_{q,k} = p_{1q} \gamma_{q,k} + p_{2q}$$

where $p_{1q}$ is the slope fit for phytoplankton strain $q$ and $p_{2q}$ is the $y$-intercept.

All HiDPs ($n = 9$) were assigned a linear fit (coccolithophores $[n = 6]$, *Phaeocystis antarctica* $[n = 2]$, and *Amphidinium carterae* $[n = 1]$) (Supporting Information Fig. S2). For those strains with intracellular DMSP measured at more than two significantly different growth rates ($n = 5$), $R^2$ values ranged from 0.05 to 0.96.

**Modeling in situ DMSP concentrations**

To assess the impact of nutrient stress on global DMSP concentration prediction, we used output from a global biogeochemical-ecosystem model. The version of the MIT ecosystem model (DARWIN) used in this study was based on Dutkiewicz et al. (2015) and contained 51 plankton types incorporating both functional and size diversity. Specifically, the ecosystem model included 35 phytoplankton types: picoprykaryotes (2 size classes), picococcolithophores (2 size classes), coccolithophores (5 size classes), diazotrophs (5 size classes), diatoms (11 size classes), and mixotrophic dinoflagellates (10 size classes). The phytoplankton were grazed by 16 size classes of zooplankton. The size classes within functional groups followed the allometric parameterizations used in Ward et al. (2012). The ecosystem was embedded in a three dimensional physical model with 18 km resolution constrained by observations (Menemenlis et al. 2008).

DMSP production was calculated for all 35 model phytoplankton types as a function of nutrient stress (Eq. 3–8) using 3-d average surface nutrient and biomass fields from the year 2000. The year 2000 was chosen as a representative “generic” year with no significant El Niño or La Niña effects. The picoprykaryotes, diazotrophs, and diatoms were classified as LoDPs. The picococcolithophores, coccolithophores, and dinoflagellates were classified as HiDPs. Growth limitation due to nutrient stress for each phytoplankton type ($j$) for each model grid cell was calculated as the most limiting nutrient ($i$) after Dutkiewicz et al. (2015):

$$\gamma_j = \min(N_{\text{lim}ji})$$

where $N_{\text{lim}ji}$ is the half-saturation constant for nutrient $i$ for phytoplankton type $j$. Nitrogen limitation in the model takes the form:

$$N_{\text{lim}ji} = \frac{N_i}{N_i + \kappa N_{ij}}$$

where $N_i$ is the nutrient concentration and $\kappa N_{ij}$ is the half-saturation constant for nutrient $i$ for phytoplankton type $j$.

Nitrogen limitation in the model takes the form:

$$N_{\text{lim}ji} = \frac{N_i}{N_i + \kappa N_{ij}}$$

where $\kappa N_{ij}$ is the half-saturation constant of inorganic nitrogen ($NO_3 + NO_2$), $\kappa_{nh4j}$ is the half-saturation constant of NH$_4$, and $\psi$ reflects the fixed nitrogen uptake inhibition by ammonia.

Intracellular DMSP concentrations were then calculated for each phytoplankton type in each model grid cell using the derived equations for the relationship between intracellular DMSP and growth limitation (Eqs. 2–4) and the modeled growth limitation (Eq. 5). For functional groups with multiple strain specific relationships (picococcolithophores, diatoms, coccolithophores, and dinoflagellates; Supporting Information Figs. S1, S2), the intracellular DMSP concentration was calculated for each relationship and then the average predicted intracellular concentration was used. As there were no published studies on intracellular DMSP under nutrient limitation for the picop Prykaryotes, *Synechococcus*, and *Prochlorococcus*, we used the response reported for *Trichodesmium* (an organism with very different ecological importance but similar intracellular DMSP concentrations) (Supporting Information Fig. S1). In DARWIN, nutrient half-saturation constants varied as a function of cell size such that larger cells experienced more nutrient limitation than smaller cells within the same group. This yielded a range of intracellular DMSP quotas within each functional group. Finally, water column DMSP concentration was calculated for each model grid cell as:

$$\text{DMSP}_{p} = I_{i}^* \text{vol}_{i}^* \frac{1}{Q_{i}} \* X_{j}$$

where $I_i$ is the intracellular DMSP for phytoplankton type $j$, $\text{vol}_{i}$ is the assigned biovolume ($\mu$m$^3$) for $j$, $Q_i$ is the assigned carbon quota for $j$, and $X_j$ is the modeled biomass of $j$ (mmol C m$^{-3}$). Values for half saturation constants, cell volume, and cellular carbon quota of the 35 phytoplankton types are provided in Supporting Information Table S3.

**Global DMSP database**

The global distribution of DMSP estimated using DARWIN output was compared against observed surface DMSP concentrations (< 10 m) from the PMEL database (https://saga.pmel.noaa.gov/dms/). Due to the paucity of DMSP observations, we relied upon DMSP measurements to validate the global patterns predicted by the model. DMSPt is a reasonable proxy for DMSP global patterns as DMSP typically comprises > 90% of the DMSP pool (Kiene and Sleazak 2006). We excluded studies that followed an acidification protocol for samples with a high abundance of *Phaeocystis* ($n = 145$) (creating significant overestimation, del Valle et al. 2011) and samples collected in harbors, estuaries, or with water column depths < 200 m ($n = 207$) (Gali et al. 2015). We also added a new dataset ($n = 13$) from a transect in the equatorial western Pacific in 2015, an under-sampled area for DMSP measurements.
After curating the dataset, there were a total of 4210 DMSPp measurements.

**Time-series in situ data**

The methodology described above for estimating in situ DMSPp based on community composition and nutrient stress response curves was used to calculate DMSPp at two time-series sites with well-characterized seasonal DMSPp dynamics: the Bermuda Atlantic Time series Site (BATS) (25.9°N, 58.7°W) in the subtropical North Atlantic from August 2007 to September 2008, and the Antarctica LTER Palmer Station B (Palmer) (64.78°S, 64.07°W) from November 2005 to February 2006. BATS is a low productivity, oligotrophic site while Palmer is a high-productivity site with a classic spring/summer bloom. HPLC pigments, chlorophyll a (Chl a), and particulate organic carbon (POC) measurements corresponding to the days DMSPp was measured were extracted from respective databases (http://batsftp.bios.edu/, accessed 18 December 2017, https://oceaninformatics.ucsd.edu/datazoo/catalogs/palmer/, accessed 17 March 2018).

Equation 8 was used to predict DMSPp at both time-series sites. $X_i$ (total carbon biomass of functional group $j$) was estimated from HPLC pigment concentrations. At BATS, the HPLC algorithms of Andersen et al. (1996) that have been validated for the BATS site were used to estimate group specific Chl a concentrations of prochlorophytes and diatoms (assigned to be LoDPs) and prymnesiophytes, pelagophytes, and dinoflagellates (assigned to be HiDPs). At Palmer, the

![Fig. 1. Tree of representative prokaryotic (left) and eukaryotic (right) DMSP producers built with 16S and 18S phylogeny. The prokaryotic producers are grouped by functional groups, while the eukaryotic producers are grouped by the major eukaryotic supergroups. Blue text represents LoDP’s (intracellular DMSP < 50 mM) and red text represents HiDP’s (intracellular DMSP > 50 mM).](image-url)
site-specific HPLC CHEMTAX ratios (Kozlowski et al. 2011) were used to estimate Chl a of flagellates and diatoms (assigned to be LoDPs) and prasinophytes, cryptophytes, and Phaeocystis (assigned to be HiDPs). Group-specific Chl a was converted to carbon using in situ measured POC : Chl a ratios. As group specific POC : Chl a ratios were not available, the median POC : Chl a at Palmer of 146 was used. At BATS, seasonality of POC : Chl a was found to be important for accurate DMSPP prediction and therefore seasonally varying POC : Chl a based on observed values were used (see Supporting Information Fig. S3 for details). Group specific carbon was then converted to biovolume using the biovolume : carbon quota ratio for the corresponding functional group in the DARWIN model (see Supporting Information Table S4 for constants). Finally, DMSPP was predicted (Eq. 8) using the estimated biovolume m⁻³ for each group (vol_i * X_i) and the modeled intracellular DMSPP of each group (i_j in Eq. 8) calculated using the nutrient stress for each site estimated by DARWIN. Predicted DMSPP production by each group was summed and concentrations were compared against monthly measured DMSPP concentrations during an entire seasonal cycle at BATS (Levine et al. 2015) and against approximately biweekly DMSPP measurements during the Antarctic field season (November–February) at Palmer (Herrmann et al. 2012).

Results

Diversity of DMSP producers

A compilation of all published studies and our own measurements demonstrated a much greater diversity in DMSP producers than previously assumed (Keller et al. 1989), with over 50% of these DMSP producers classified as LoDPs (n = 113 of 216 total) (Fig. 1, Supporting Information Table S1). The major eukaryotic supergroups Rhizaria, Chromalveolate, and Archaeoplastid all have many confirmed DMSP producing representatives. The absence of representatives from the unikont and excavate supergroups does not imply these groups lack the ability to produce DMSP, but rather a lack of measurements for these groups. Though often overlooked, a diverse array of prokaryotic groups has also been shown to produce DMSP, including cyanobacteria, purple sulfur bacteria, purple non-sulfur bacteria, and alphaproteobacteria (Karsten et al. 1996; Curson et al. 2017) (Fig. 1). Critically, four key photosynthetic marine cyanobacteria (Synechococcus, Prochlorococcus, Trichodesmium, and Crocosphaera) have all been shown to produce DMSP (Corn et al. 1996; Bucciarelli et al. 2013; this study), albeit with extremely low-intracellular concentrations. The diversity of DMSP producers highlighted by this compilation suggests a potentially deep rooted evolution of the DMSP synthesis pathway as DMSP is found in many prokaryotic phyla belonging to ancient lineages (Fig. 1). This is consistent with the phylogeny of the recently identified prokaryotic DMSP synthesis gene (dySB) and eukaryotic DMSP synthesis gene (DYSB) (Curson et al. 2017, 2018).

Meta-analysis

To identify over-arching trends in DMSP regulation by LoDPs and HiDPs in response to environmental stress, we analyzed the previously reported response of 19 different strains of phytoplankton to seven different types of nutrient limitation (Supporting Information Table S2). Comparing across previous studies is complicated due to fundamental differences in methodologies: strains studied, growth conditions, and normalization factor. In particular, the use of different biomass normalizations can create very different results even within the same study as nutrient stress affects multiple components of cellular physiology, not just cellular DMSP regulation. For example, Thalassiosira oceanica grown under iron limitation showed a 12-fold increase in DMSP when normalized to cell volume, a 40-fold increase when normalized to Chl a, but only a 1.2-fold increase when normalized to cell carbon (Bucciarelli et al. 2013). To remove this effect, only studies reporting intracellular DMSP (normalized to cell volume) were included in our analysis. In addition, to facilitate comparison across studies, we analyzed results in terms of growth limitation (γ, nutrient stressed growth rate relative to replete growth rate) and the fold change in DMSP production (nutrient stressed intracellular DMSP concentrations relative to replete concentrations). Despite large differences in culturing techniques and nutrient limitations, similar responses were seen across the seven different types of nutrient limitations with consistent differences observed between HiDPs and LoDPs (Table 1).

The average intracellular DMSP concentration for HiDPs under significant limiting conditions of γ < 0.5 (253 ± 120 mM DMSP) was not significantly different than the average concentration under replete conditions (224 ± 127 mM DMSP, t-test p > 0.1). The high variability in the average intracellular DMSP for HiDPs (Fig. 2) was primarily driven by the large range of intracellular DMSP concentrations for 10 coccolithophore species (range of 174–715 mM DMSP) reported by Franklin et al. (2010). The average intracellular DMSP concentration for LoDPs under the same limiting conditions (23 ± 16 mM DMSP) was significantly higher than the average intracellular DMSP under replete conditions (8 ± 14 mM DMSP, t-test p = 0.004) (Fig. 2). While intracellular DMSP concentrations of LoDPs were much lower than those of HiDPs, the LoDPs’ intracellular DMSP concentrations under nutrient stress begin to approach those of the HiDPs, with a maximum of 67 mM intracellular DMSP reported for Skeletonema marinoi (Spielmeyer and Pohnert 2012) (Fig. 2).

LoDPs showed an average fold change in intracellular DMSP of 16 ± 19 in response to significant nutrient stress (γ < 0.5) (Fig. 2; Table 1), with a maximum fold change of 73 by Thalassiosira pseudonana in response to CO₂ limitation (Sunda et al. 2002). In contrast, the HiDPs showed both a
smaller fold change and a less variable response of $1.4 \pm 0.5$, with a maximum fold change of 2.6 by *Emiliania huxleyi* in response to CO$_2$ limitation (Sunda et al. 2002) (Fig. 2; Table 1). Differences in experimental design and degrees of nutrient limitation employed across these studies most likely contributed significantly to the highly variable fold changes for LoDPs. Despite this variability, we found the strong upregulation of intracellular DMSP by LoDPs to be highly predictable as a function of $\gamma$ for every study and strain tested ($n = 11$) (Fig. 3, Supporting Information Fig. S1). In contrast, the low variability in HiDP fold changes, despite similar differences in experimental design, strongly supports a lack of a DMSP response by HiDPs to nutrient stress. Unlike LoDPs, a predictable increase in intracellular DMSP as a function of $\gamma$ was not found for HiDPs ($n = 9$), and some studies even showed a slight decrease of intracellular DMSP with decreasing $\gamma$ (Fig. 3, Supporting Information Fig. S2).

The aim of this study was to identify overarching trends in DMSP regulation by HiDPs and LoDPs in response to nutrient stressors. However, for completeness, an analysis of the available data for the response to temperature, light, and global change stressors are included in the Supporting Information S1. The response of HiDPs to non-nutrient stressors was similar to the nutrient stress response. Further studies quantifying the response of LoDPs to non-nutrient stressors are needed to understand how these stressors might impact DMSP production by this group and how this differs from the HiDP response.

### Predicted DMSPp in high- and low-productivity regions

To assess the contribution of a nutrient stress response to variability in in situ DMSPp concentrations and to estimate the potential contribution of LoDPs to in situ DMSPp, the observed relationship between growth limitation and intracellular DMSP was used to predict surface DMSPp at two time-series sites. Good agreement was observed at both Palmer and BATS (Fig. 4) between in situ predicted and observed DMSPp temporal patterns ($R^2 = 0.8$, $p < 0.001$ at Palmer, $R^2 = 0.4$, $p = 0.09$ at BATS).

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**Table 1.** The average and maximum fold changes for HiDPs and LoDPs in response to six different nutrient limitations ($n =$ number of data points analyzed) with a significant reduction in growth limitation due to nutrient stress ($\gamma < 0.5$).

| Nutrient | HiDP Average fold change | LoDP Average fold change | HiDP Maximum fold change | LoDP Maximum fold change |
|----------|--------------------------|--------------------------|--------------------------|--------------------------|
| NO$_3$   | $1 \pm 0.3$              | $14 \pm 2$               | $2$                       | $29$                      |
| Fe       | $2 \pm 0.5$              | $37 \pm 31$              | $3$                       | $73$                      |
| CO$_2$   | $1 \pm 0.5$              | $19 \pm 3$               | $2$                       | $45$                      |
| $k$/50   | $--$                     | $--$                     | $2$                       | $--$                      |

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**Fig. 2.** (a) Intracellular DMSP reported for HiDP’s and LoDP’s when $\gamma < 0.5$. Black dashed line represents the 50 mM boundary between HiDP’s and LoDP’s. (b) Fold change in HiDP’s and LoDP’s intracellular DMSP under $\gamma < 0.5$ relative to replete growth. Black dashed line of 1 represents no response to nutrient limitation.
p = 0.02 at BATS, Supporting Information Table S5). Assumptions for predicting biomass from HPLC pigments (see “Methods” section) and the use of average intracellular DMSP fits most likely contributed to divergences between predicted and measured DMSPp. Good agreement was also observed between our mechanistic prediction of DMSPp and the empirical algorithm from Galí et al. (2015) at Palmer ($R^2 = 0.95$, $p < 0.0001$) (Supporting Information Fig. S4). At BATS, while both the DARWIN and Galí et al. predictions showed similar root mean squared error when compared against in situ observations, there was no relationship between the two predictions or between Galí et al. and the in situ measurements (Supporting Information Table S5). The ability of the DARWIN prediction to better match important temporal features of DMSPp at BATS relative to Gali et al. (Supporting Information Fig. S4) and Table S5) suggests that explicit incorporation of nutrient stress and/or community composition is important for predicting in situ DMSPp variability in low-productivity, oligotrophic regions.

As expected, the high-productivity site (Palmer) never showed significant growth limitation in the DARWIN model and $\gamma$ was always predicted to be > 0.9. As a result, intracellular DMSP was always at a minimum for all phytoplankton types and variability in in situ DMSPp was driven by shifts in community composition. During the primary DMSPp maximum (predicted to be > 400nM), a cryptophyte (HiDP) bloom accounted for 46% of total biomass and was estimated to have produced 77% of total DMSPp (Fig. 4). During the secondary maxima (16–30 January 2006), the LoDPs (diatoms and flagellates) dominated more than 90% of the total biomass, and yet, the HiDPs were still estimated to produce an average 66% of the total DMSPp during this period.

In contrast, at the low-productivity site (BATS), average $\gamma$ for all phytoplankton types varied from a maximum of 0.7 during the winter to a community averaged minimum of 0.04 during the summer in DARWIN. This resulted in upregulation of DMSPp by both LoDPs and HiDPs during the summer. However, the large upregulation of LoDP intracellular DMSP due to nutrient stress was not enough to result in a significant contribution to in situ DMSPp. For example, prochlorophytes (LoDPs) dominated the community (an average 53% of total biomass throughout the year, and maximum of 87%), but were only estimated to contribute a maximum 7% of total DMSPp (Fig. 4). Diatoms experienced the most extreme growth limitation ($\gamma \sim 0.01$) but never contributed more than 1% of total DMSPp. Instead, similar to Palmer, the HiDPs at BATS (pelagophytes, prymnesiophytes, and dinoflagellates) were estimated to dominate DMSPp production, accounting for 97% of the total seasonal DMSPp produced. These two examples suggest that our single set of equations incorporating differential nutrient response for HiDPs and LoDPs may allow us to accurately predict in situ DMSPp for very different oceanographic regions. Furthermore, these results suggest that HiDP biomass dominates DMSPp production, even when HiDPs are the subdominant population.

To confirm the importance of community composition in determining in situ DMSPp, we also estimated DMSPp for the
two sites using total Chl a (Supporting Information Fig. S4). As has been shown previously (e.g., Toole and Siegel 2004), the Chl a based estimate was able to reproduce the majority of the variability observed in the high-productivity region, but was unable to capture the dynamics in the low-productivity region. Indeed, total Chl a at Palmer was significantly correlated with observed DMSPp, while there was no relationship at BATS (Fig. 5). We propose that the linear relationship between DMSPp and Chl a in high-productivity regions is a result of Chl a being a good proxy for HiDP biomass in these regions ($R^2 = 0.6$, $p < 0.001$ for Chl a vs. HiDP cellular biovolume at Palmer). In fact, a correlation was observed between DMSPp and HiDP cellular biovolume concentrations ($\mu$L cell $L^{-1}$) for both sites (Fig. 5). At BATS, the weaker relationship was expected due to uncertainties in our assumptions (i.e., C : Chl a ratios, biovolume, and cellular carbon quota) that introduce greater uncertainty in the estimate of HiDP cellular biovolume at low-biomass concentrations than at Palmer where total biomass is an order of magnitude greater (note x-axes of Fig. 5). Despite an order of magnitude difference in the observed range of DMSP concentrations, the slopes of the linear relationship between DMSPp and HiDP cellular biovolume at both time-series sites were not statistically different ($p = 0.2$, Z-test statistic) and were equivalent to typical HiDP intracellular DMSP concentrations (Fig. 5). This provides evidence that a single set of equations for predicting DMSPp based on HiDP cellular biovolume is justified even in contrasting high- and low-productivity regions. Furthermore, potential stress mechanisms, including $\gamma$ at Palmer and BATS (Fig. 5) and upper mixed layer UV light dose at BATS (Supporting Information Fig. S5), were not significantly correlated with in situ DMSPp. This again suggests that environmental stress plays a secondary role to community composition in driving in situ DMSPp variability.

**Modeled global DMSPp**

Spatial and temporal differences in the contribution of nutrient stress and HiDPs and LoDPs to global patterns of in situ DMSPp were assessed using the DARWIN model. The DARWIN-based estimates of DMSPp captured the critical spatial and temporal features in observed in situ DMSPt concentrations (Fig. 6, Supporting Information Fig. S6). Specifically, the model estimates captured the observed elevated DMSPp concentrations in the high latitude spring and upwelling regions, and the low DMSPp concentrations in oligotrophic gyres (Fig. 6), as well as temporal features in oceanographic provinces (Supporting Information Fig. S6). A significant linear relationship was observed between DARWIN predicted DMSPp and in situ measured DMSPt observations binned by HiDP community composition as predicted by DARWIN (Fig. 7). However, predicted DMSPp was both underestimated relative to observations with a mean relative bias of $-53\%$ and showed significantly lower variability (Figs. 6, 7).

Differences between the observed and modeled predictions of DMSP were expected as interannual variability in the timing and spatial location of blooms and shifts in community composition are not captured by the DARWIN model output for a single average year. In high-productivity regions, the model-observation differences were attributed to a sampling bias in the observational dataset toward spring bloom measurements (Galí et al. 2018), spatial averaging or an underestimate of the magnitude of spring blooms in the model, and mismatches in community composition between the model and in situ data. Blooms are often patchy and driven by
fine-scale processes (e.g., Mahadevan et al. 2012) that are typically not captured by large-scale models (Hashioka et al. 2013). Specifically, DARWIN predicted DMSPp represents the "mean state" (averaged over 3-d and 18 km) and therefore does not capture fine-scale variability and elevated Chl that are observed during blooms. Finally, the lack of a Phaeocystis functional group in DARWIN, particularly in the Antarctic where diatoms (LoDPs) compensate for this ecological niche, contributed substantially to DMSPp underestimation in the model (Wang et al. 2015). Underestimates in oligotrophic regions are primarily attributed to an underestimate of HiDP biomass when these groups were the subdominant phytoplankton community. In DARWIN, cyanobacteria (picoproteobacteria and diazotrophs) dominated phytoplankton biomass (~50–100%) in oligotrophic regions (Supporting Information Fig. S7) and HiDP phytoplankton types appeared to be underestimated based on a comparison to HPLC pigments at BATS.

As observed at the Palmer and BATS time-series sites, HiDP biomass is the primary determinant of in situ DMSPp concentrations in all oceanographic regions (Fig. 7). Specifically, the biomass of the 17 HiDP phytoplankton types contributed 96% of the predicted in situ DMSPp concentrations. In areas of high DMSPp production, mainly upwelling regions and frontal zones, coccolithophores and dinoflagellates dominated DMSPp production. In oligotrophic regions, the picoeukaryotes were the most abundant HiDP and so dominated DMSPp production (e.g., at BATS in DARWIN, picoeukaryotes produced 81% of the total DMSPp in August). The importance of picoeukaryotes for oligotrophic DMSPp production in our predictions supports the findings of Gali et al. (2015), which also suggested an assignment of HiDP to the picoeukaryote functional group despite having very few measurements of cellular DMSP (Supporting Information Table S1) for this important group (Massana 2011). The modeled relationship between HiDP community composition and DMSPp concentration was also observed in the in situ dataset where samples with a higher fraction of HiDP (predicted by DARWIN) had higher measured DMSPt than samples with a lower fraction HiDP (Fig. 7).
LoDP mean intracellular DMSP concentrations were greatly upregulated in the oligotrophic oceans due to nutrient stress as expected, 56-fold, 10-fold, and 62-fold for picoprokaryotes, diazotrophs, and diatoms, respectively. HiDPs upregulated intracellular DMSP in these regions as well, but never as drastically as the LoDPs with a maximum 1.4-fold, 1.6-fold, and 1.6-fold upregulation by picoeukaryotes, coccolithophores, and dinoflagellates, respectively. Despite a small response to nutrient stress, HiDPs dominated the increase in DMSPp inventory due to nutrient stress. Specifically, 76% of the global increase in DMSPp due to nutrient stress was associated with the small upregulation of HiDP intracellular DMSP. Including nutrient stress in modeled DMSPp resulted in an average 1.8 nM increase in in situ DMSPp (a 28% increase) relative to estimates using only community composition (i.e., assigning HiDPs and LoDPs stagnant replete laboratory intracellular quotas as done previously; Le Clainche et al. 2010) (Fig. 8). LoDP intracellular DMSP was always at a maximum in the oligotrophic ocean, but the magnitude of this upregulation was not great enough to compensate for the inherently lower intracellular DMSP. Thus, LoDPs did not contribute significantly to predicted DMSPp (annual average 4%). In fact, the highest contribution of DMSPp by LoDPs was found not in the nutrient limited oligotrophic oceans, but in the regions where these phytoplankton types were most abundant.

Of the LoDPs, diatoms had the most potential to contribute to in situ DMSPp due to their higher intracellular DMSP content relative to the other LoDP phytoplankton types (Supporting Information Fig. S1), their larger size, which made them more nutrient limited in the model, and their ability to achieve higher biomass values (blooms) in the model. However, the maximum contribution by diatoms to total DMSPp was 2 nM in the equatorial upwelling region (or 5.9 nM if only the response for Skeletonema marinoi was used; Fig. 3). While these results suggest that environmental (nutrient) stress is not the first-order mechanism for predicting trends in global DMSPp, it was important for accurately representing the contribution by LoDPs. Without incorporating this mechanistic upregulation (Fig. 3), contribution to global DMSPp by LoDPs would be much less (annual average 1.8%).

Fig. 6. Seasonal mean predicted DMSPp for (a) winter (December–February), (b) spring (March–May), (c) summer (June–August), (d) fall (September–November). Overlay of points represent measured DMSPt from the curated PMEL database from the same months. Note the maximum 50 nM of the scale bar is much lower than the maximum observed in situ DMSPt (see Fig. 7). The scale was capped to facilitate comparison of spatial and temporal trends between model and observations.
The high intracellular DMSP of HiDPs with little regulation suggests constant, constitutive production by this group. By contrast, the active regulation of intracellular DMSP in response to nutrient limitation by LoDPs appears to be an acute stress response (Fig. 2), but the mechanism (overflow, antioxidant, or signaling molecule) remains to be confirmed.

These contrasting dynamics suggest different physiological roles for DMSP in LoDPs and HiDPs. For example, the strong regulation and low-intracellular concentrations of DMSP in LoDPs are not consistent with DMSP being a major osmolyte for this group. Specifically, we estimate that DMSP could only contribute 0.004–5% of total osmolarity in LoDPs (see Supporting Information S2 for calculation details). On the other hand, intracellular DMSP in HiDPs could account for 14–34% of total osmolarity. Similarly, substitution of DMSP for high nitrogen content osmolites under nitrogen limitation (e.g., glycine betaine; Keller et al. 2004; Bertrand and Allen 2012), could only alleviate 0.6% and 7% of LoDP and HiDP’s cellular nitrogen requirements, respectively (see Supporting Information S2 for calculation details). These calculations suggest that, even under nutrient limitation, regulation of DMSP could only serve a significant role in osmotic balance for HiDPs. However, despite a lack of regulation, DMSP could still be serving to protect HiDP cells against environmental stressors, as high intracellular DMSP concentrations in HiDPs may not require the drastic upregulation seen in LoDPs to deal with radical quenching (Sunda et al. 2002; Lavoie et al. 2016).

Different physiological roles for DMSP in LoDPs and HiDPs are consistent with recent genomic insight which suggests there may be multiple eukaryotic DMSP synthesis genes. Of the 53 species with DYSB hits in Curson et al. (2018), 46 are known or related to HiDPs and none of the confirmed LoDPs examined in this study appear to harbor DYSB. The LoDP gene may be related to a candidate protein recently described for DMSP synthesis in Thalassiosira pseudonana.
other stressors; not altering our conclusion that for nutrients (Supporting Information S1), and including these stressors suggests the response is comparable to that observed in our calculations due to insufficient data. To determine the DMSP synthesis genes of other organisms not predicted to contain dysB, DYSB, or TpMMT (e.g., Trichodesmium). Future studies incorporating direct measurements of DMSP synthesis (Stefels et al. 2009; Archer et al. 2017) with genomic measurements (Curson et al. 2017, 2018) will help decipher the physiological mechanisms behind differential LoDP and HiDP regulation.

While constraining the physiological mechanisms of DMSP for different phytoplankton types is critical for understanding the ecological roles of DMSP, simply differentiating between the two different types of DMSP producers was sufficient for reproducing the major role of nutrient spatial and temporal dynamics of in situ DMSP concentrations. In particular, our calculations captured the observed decoupling between Chl a and DMSP in a low-productivity region (Fig. 4), which previous models struggle to replicate. The model presented here provides two important improvements on our ability to predict global DMSP. First, we apply a single set of equations to multiple oceanographic regimes and do not rely on the definition of different biogeochemical regimes or thresholds for a stress response. This is especially critical for future predictions as these thresholds might change with shifts in the climate. Second, we use the observed responses from a large number of laboratory monoculture experiments to model intracellular DMSP regulation due to nutrient stress in multiple phytoplankton types. Most previous models either used fixed DMSP : carbon ratios or a single relationship between cellular DMSP and environmental stress (light, nutrients, and/or temperature) for all phytoplankton types (Le Claire et al. 2010; Vogt et al. 2010).

By including a mechanistic representation of the differential regulation of DMSP in response to nutrient stress, we were able to quantitatively evaluate the relative importance of nutrient stress in determining variability in DMSPp concentrations (Fig. 8). We demonstrate that nutrient stress most likely plays a minor role in determining spatial and temporal patterns of in situ DMSPp concentrations (Fig. 5). Other environmental stressors have been shown to impact DMSP production through upregulation (e.g., temperature stress) or downregulation (e.g., acute UV stress) but were not included in our calculations due to insufficient data. A survey of the current state of knowledge on the impact of these other stressors suggests the response is comparable to that observed for nutrients (Supporting Information S1), and including these other stressors would not alter our conclusion that community composition is the primary driver of variability in DMSPp concentrations.

The dominant role of community composition in predicting DMSPp found in this study may appear contradictory to previous studies that required environmental stress parameterizations to predict in situ DMSP in oligotrophic regions. However, we hypothesize that the impact of environmental stress implicitly accounted for shifts in community composition. For example, many studies used light stress to improve in situ DMSP predictions in oligotrophic regions. However, seasonal changes in light stress co-occur with community composition shifts (e.g., Polimene et al. (2012)) and thus implicitly incorporate this dominant mechanism. Similarly, the remote-sensing-based algorithms developed by Gali et al. (2015) divide DMSPp production into two different regime types (stratified and mixed water columns), which also implicitly included shifts in community composition. These methodologies were overall successful, but an explicit representation of HiDP and LoDP abundance used here provides a mechanistic representation of these dynamics and improved predictions of temporal dynamics in oligotrophic regions.

This work highlights that the primary challenge for robust predictions of in situ DMSP is accurately capturing the dynamics of the subdominant phytoplankton community, specifically that of the HiDP phytoplankton types. This is a significant challenge both for numerical ecosystem models and for remote-sensing algorithms which have been shown to successfully capture the dominant phytoplankton type (e.g., Alvain et al. 2008; Dutkiewicz et al. 2015) but struggle to accurately predict the biomass of groups that make up a small fraction of the community. This is particularly problematic in the DARWIN oligotrophic and polar (> 60°) communities, where the dominant DMSP producers are outcompeted. Slight changes in HiDP biomass for these regions would result in large changes in water column DMSP. For example, to produce a water column of 15 nM DMSPp, a drop of seawater (1 μL) would require 15 small (48 μm3) diatom cells (γ = 0.01, 22 mM intracellular DMSP), but less than 1 cell of the same size coccolithophore (γ = 0.03, 354 mM intracellular DMSP). The large range of intracellular DMSP content within species of the same genus (e.g., Franklin et al. 2010, range from 174 mM DMSP to 715 mM DMSP) further complicates this estimate as species or even strain level shifts could significantly impact in situ DMSP.

While the impact of the subdominant HiDP community on in situ DMSP production has been observed before, there has been no direct assessment of its role as a driving mechanism in DMSP predictions in global ecosystem models or satellite algorithms. Masotti et al. (2010) encountered similar difficulties with poorly resolved subdominant communities when investigating global trends in DMSP. The authors found that certain regions dominated by LoDP phytoplankton types according to the PhySAT algorithm were associated with unexpectedly high, in situ measurements of DMSP : Chl a ratios and
concluded that these ratios must be driven by the subdominant HiDP groups. Here, our calculations provide direct support for this finding. Phytoplankton types designed to represent DMSPp dynamics would greatly improve the prediction power of DMS(P) in global models (Stefels et al. 2007; Gali et al. 2015), but only if the model was able to accurately capture the coexistence of these groups when they make up a small fraction of the biomass. Similarly, this analysis suggests that improved remote-sensing-based algorithms that robustly estimate the subdominant community will significantly improve our ability to predict DMSPp using algorithms similar to Gali et al. (2015).

Conclusion

The ability to synthesize DMSP is widespread throughout the tree of life and includes both eukaryotes and prokaryotes (Fig. 1). Furthermore, our analysis suggests that LoDPs are most common and might outnumber HiDPs. Our meta-analysis provides evidence for the hypothesis presented by Stefels et al. (2007) that there are two distinct mechanisms for DMSP regulation. Specifically, HiDPs appear to maintain constitutive DMSP production while LoDPs actively regulate intracellular DMSP in response to nutrient stress. We hypothesize that different DMSP synthesis genes in the two groups may encode these differences.

Using the observed upregulation of DMSP in response to nutrient stress, we tested the hypothesis that LoDPs might contribute significantly to in situ DMSP (Bucciarelli et al. 2013). We show that LoDPs cannot produce environmentally relevant DMSPp concentrations, even in regions of very high productivity (e.g., Palmer) or regions of extreme nutrient stress (e.g., oligotrophic regions). While less environmentally relevant on a global scale, the maintenance of the genetic machinery for DMSP synthesis by LoDPs suggests that DMSP serves an important physiological function in these cells. In particular, significant changes in DMSP due to nutrient stress in oligotrophic environments indicate that DMSP may be required for survival if limited resources are being used to upregulate DMSP synthesis. DMSP is known to play an important role in microscale organic carbon and sulfur cycling within the phyecosphere and could serve as a signaling molecule in the open oceans (Seymour et al. 2010, 2017; Johnson et al. 2016). It is plausible that the environmental significance of DMSP production by LoDPs is confined to a much smaller scale within the phyecosphere, where LoDPs “trade” DMSP for limiting nutrients with associated heterotrophic bacteria (Amin et al. 2015; Seymour et al. 2017). A similar relationship has been observed for a different organosulfur compound (2,3-dihydroxypropane-1-sulfonate) both in monocultures and in situ (Durham et al. 2015, 2017), but remains to be observed for DMSP.

The inherently higher intracellular DMSP of HiDPs, particularly coccolithophores, dinoflagellates, and Phaeocystis, dominates global DMSPp production even when these groups are the subdominant community. This study highlights the importance of accurately representing the subdominant community in order to accurately capture in situ DMSPp dynamics. Even with the 35 phytoplankton types in DARWIN, over-estimation of the biomass of the dominant phytoplankton type added uncertainty to DMSPp predictions. Future work to better capture the dynamics of subdominant communities will be critical for improving predictions of both DMSPp dynamics and, most likely, other biogeochemically important metabolites whose cycling is primarily driven by a small fraction of the community.

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Conflict of Interest

None declared.

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