

Cryptic carbon and sulfur cycling between surface ocean plankton

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About half the carbon fixed by phytoplankton in the ocean is taken up and metabolized by marine bacteria, a transfer that is mediated through the seawater dissolved organic carbon (DOC) pool. The chemical complexity of marine DOC, along with a poor understanding of which compounds form the basis of trophic interactions between bacteria and phytoplankton, have impeded efforts to identify key currencies of this carbon cycle link. Here, we used transcriptional patterns in a bacterial-diatom model system based on vitamin B₁₂ auxotrophy as a sensitive assay for metabolite exchange between marine plankton. The most highly up-regulated genes (up to 374-fold) by a marine Roseobacter clade bacterium when cocultured with the diatom *Thalassiosira pseudonana* were those encoding the transport and catabolism of 2,3-dihydroxypropane-1-sulfonate (DHPS). This compound has no currently recognized role in the marine microbial food web. As the genes for DHPS catabolism have limited distribution among bacterial taxa, *T. pseudonana* may use this sulfonate for targeted feeding of beneficial associates. Indeed, DHPS was both a major component of the *T. pseudonana* cytosol and an abundant microbial metabolite in a diatom bloom in the eastern North Pacific Ocean. Moreover, transcript analysis of the North Pacific samples provided evidence of DHPS catabolism by Roseobacter populations. Other such biogeochemically important metabolites may be common in the ocean but difficult to discriminate against the complex chemical background of seawater. Bacterial transformation of this diatom-derived sulfonate represents a previously unidentified and likely sizeable link in both the marine carbon and sulfur cycles.

bacteria | diatoms | DHPS | sulfonates | vitamin B12

Carbon-cycle-relevant interactions between heterotrophic marine bacteria and phytoplankton are mediated through compounds excreted from living phytoplankton cells or released when the cells are grazed or lysed (1). Current views of these interactions are rooted in the idea of passive trophic transfer to heterotrophic bacteria, although recent findings of pathogen-like genes in bacterial genomes (2) and predictable associations between microbial taxa (3, 4) suggest that more strategic interactions link autotrophic and heterotrophic plankton. Compounds serving as intermediates in bacterial-phytoplankton interactions are likely to be present in low concentration or to reach high concentration only within the cells' diffusive boundary layers (5, 6) and in either case are difficult to discriminate over the complex chemical background of seawater. To the extent that these compounds remain unrecognized as currencies of trophic interactions, particularly when abundant plankton groups are involved, they represent gaps in our understanding of marine elemental cycles.

We established a model microbial system for exploring bacterial-phytoplankton exchanges in which the marine bacterium *Ruegeria pomeroyi* DSS-3 had an obligate dependency on the diatom *Thalassiosira pseudonana* CCMP1335 for fixed carbon while the diatom obtained an essential vitamin from the

bacterium. As is common among marine eukaryotic phytoplankton, *T. pseudonana* harbors the B₁₂-requiring version of the methionine synthase gene (*metH*) yet cannot synthesize B₁₂ (7) and must obtain it from an exogenous source. The >50 sequenced members of the Roseobacter lineage all carry genes for B₁₂ biosynthesis (ref. 8; www.roseobase.org). Both groups of organisms are important in the ocean, with diatoms responsible for up to 40% of global marine primary productivity (9) and roseobacters ubiquitously distributed, metabolically active (10), and commonly associated with diatoms (3).

In coculture, *R. pomeroyi* DSS-3 recovered B₁₂-limited *T. pseudonana*, restoring growth rates comparable to those of axenic cultures supplemented with exogenous B₁₂ (Fig. 1). When bacterial transcriptomes collected after 8 h of cogrowth with diatoms ($n = 4$) were compared with control incubations ($f/2$ medium, +Si, -B₁₂; $n = 2$), ten of the most highly up-regulated genes (up-regulated 56- to 374-fold) encoded proteins for the transport and catabolism of the C₃-sulfonate 2,3-dihydroxypropane-1-sulfonate (DHPS; Table S1). Eight of these genes were collocated on the *R. pomeroyi* DSS-3 chromosome and included DHPS TRAP transporter components *hpsKLM* (11), dehydrogenases *hpsNOP* for converting DHPS to (*R*)-sulfolactate, and *slcD* for converting sulfolactate to sulfofpyruvate (Fig. 2). Two genes were collocated on the bacterium's megaplasmid, including *cuyA*, which mediates conversion of cysteate to pyruvate and

Significance

In the surface ocean, organic matter released by phytoplankton and degraded by heterotrophic bacteria is a key step in the carbon cycle. Compounds important in this trophic link are poorly known, in part because of the thousands of chemicals making up marine dissolved organic matter. We cocultured a Roseobacter clade bacterium with the diatom *Thalassiosira pseudonana* and used gene expression changes to assay for compounds passed to the bacterium. A C₃-sulfonate with no previously known role in the microbial food web was identified and subsequently shown to be an abundant diatom metabolite and actively cycling compound in seawater. This work identifies a missing component of the marine carbon and sulfur cycles.

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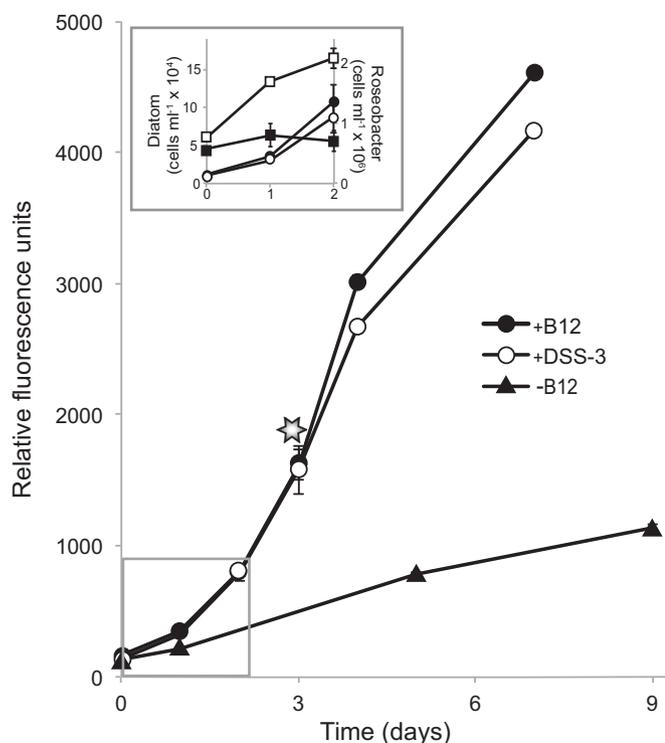


Fig. 1. Recovery of *Thalassiosira pseudonana* growth by addition of exogenous B₁₂ (filled circles) or *Ruegeria pomeroyi* DSS-3 (open circles) compared with the B₁₂-limited control (filled triangles). The star indicates the growth stage at which diatom cells were collected for RNA and metabolite analyses. (Inset) Cell counts for *T. pseudonana* following addition of exogenous B₁₂ (filled circles) or *R. pomeroyi* (open circles) and for cogenerated (open squares) or control (filled squares) *R. pomeroyi* over the first 2 d of the experiment. Error bars represent the SD of duplicate cultures.

ammonium, and the bisulfite exporter *cuyZ*. Quantitative RT-PCR (RT-qPCR) of *hpsN*, the gene encoding dihydroxypropanesulfonate-3-dehydrogenase, confirmed that providing DHPS as a sole carbon source to *R. pomeroyi* DSS-3 resulted in the same pattern of gene regulation as growth with the diatom (Fig. 2). Although the transcriptional response was strongest to DHPS, six colocated genes involved in transport and catabolism of C₂-sulfonate *N*-acetyltaurine were also up-regulated by the bacterium. (Fig. S1). The enzymatic function of these bacterial genes was established previously (11, 12), but their ecological role had remained unknown. Identification of both sulfonates as currencies in this model system suggests a diatom-derived oxidized organic sulfur pool that may be important in fueling the marine microbial food web.

Coincident changes in cocultured *T. pseudonana* CCMP1335 were assessed with poly(A)-selected transcriptomes comparing cells cultured with *R. pomeroyi* ($n = 2$) to those that were axenic but B₁₂-replete ($n = 2$) during exponential growth (Table S2). As anticipated, the gene encoding the B₁₂-binding cobalamin acquisition protein 1 (CBA1) (13) was one of the most highly up-regulated diatom genes (11-fold) when bacteria served as the source of B₁₂ compared with when the vitamin was added to the culture in excess. No other genes reported previously to be induced by B₁₂ limitation (13) were differentially regulated in the coculture. However, several sulfur-related genes were down-regulated in the diatom when cocultured with the bacterium, including *sqdB*, which mediates the first committed step in biosynthesis of the sulfolipid sulfoquinovosyl diacylglycerol (SQDG) (Tp269393; sixfold; Fig. S2), two genes involved in the synthesis of diacylglycerol precursors for SQDG biosynthesis

(Tp7093 and Tp263660; fourfold), and a gene annotated as a sulfate transporter (Tp261147; fourfold). These changes in gene expression suggest shifts in sulfur metabolism by the diatom in the presence of *R. pomeroyi*.

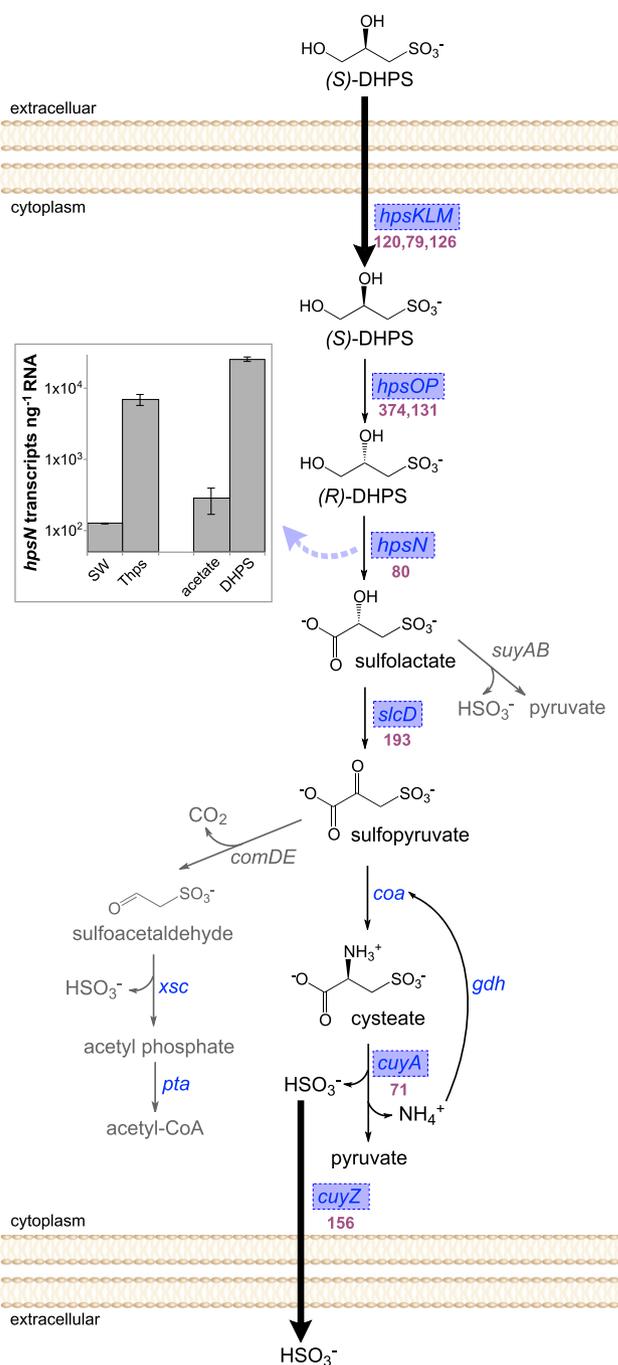


Fig. 2. DHPS transport and degradation genes in marine roseobacter *R. pomeroyi* DSS-3 (blue font) that were up-regulated (purple boxes, fold-change up-regulation indicated underneath) during coculture with *T. pseudonana*. Genes mediating metabolism of sulfopyruvate to cysteate (*coa* and *gdh*) were not differentially expressed, consistent with previous work (32). Two alternate routes of DHPS degradation present in members of the Roseobacter clade are shown in gray (Table S3). Bold arrows indicate transporters. Inset: RT-qPCR quantification of *hpsN* transcripts in *R. pomeroyi* in coculture with *T. pseudonana* (Thps; see Fig. 1, open circles) and in sterile f/2 seawater medium (SW) after 8 h, and during exponential growth with acetate or DHPS as the sole carbon source. Error bars represent SD of three technical replicates from duplicate cultures.

Some bacteria are capable of producing DHPS by degrading sulfoquinovose, the headgroup of SQDG (14). In our model system, however, the up-regulation of a dedicated DHPS transporter by *R. pomeroyi* and the previous identification of this compound in the cytosol of a freshwater diatom (15) argues that direct release of DHPS by the diatom formed the basis of the interaction. Diatoms might produce DHPS by a reductive deamination of cysteinolic acid, a potential cytosolic reservoir of reduced sulfur (16). Despite significant changes in transcription patterns, indicators of the physiological state of *T. pseudonana* (i.e., growth rate, photosynthetic efficiency F_v/F_m) showed no differences between the axenic and cocultured conditions.

The three known routes of bacterial DHPS degradation share an initial oxidation step mediated by HpsN, but carry out desulfonation via different enzymes (CuyA, SuyAB, or Xsc; Fig. 2 and Table S3). Over half of *R. pomeroyi*'s sequenced relatives in the Roseobacter clade (26 of 41 genomes) harbor at least one of the DHPS degradation pathways (Table S3), as do some marine relatives in the *Rhodobacterales* (4 of 17 genomes) and *Rhizobiales* (4 of 15 genomes) (Fig. 3 and Table S3). HpsN sequences from these alphaproteobacterial taxa form a clade that includes proteins of experimentally verified function (11). Other marine bacterial taxa that possibly harbor DHPS degradation pathways include alphaproteobacterial clade SAR116 and a limited number of marine Gammaproteobacteria (Fig. 3 and Table S3). Members of the alphaproteobacterial SAR11 clade also have a possible HpsN protein, but the sequences have an unresolved evolutionary relationship with experimentally verified sequences even when accounting for the substantial compositional heterogeneity due to differences in G+C content of the corresponding genes (Fig. 3, Fig. S3, and Table S4); further, the SAR11 genomes lack orthologs to metabolically upstream genes *hpsO* and *hpsP* (Table S3). All sequenced members of the Roseobacter clade and most of the marine *Rhizobiales* and the other marine *Rhodobacterales* that harbor a DHPS degradation pathway also have a B_{12} biosynthetic pathway (8, 17) (Table S3), whereas B_{12} biosynthesis is not nearly as widespread in the candidate DHPS-degrading SAR116 and Gammaproteobacteria taxa (<20%) and is absent in the SAR11 clade. Several taxa of soil bacteria, including strains associated with root nodules in plants, have DHPS pathway orthologs (Table S3), suggestive of similar sulfonate-based interactions between heterotrophic bacteria and terrestrial primary producers.

Whether the release of unique organic metabolites by *T. pseudonana* and other phytoplankton is used to enable mutualisms with vitamin-supplying or otherwise beneficial bacteria, or is simply excretion of excess materials that are subsequently scavenged, is a matter of debate (18, 19). In the case of DHPS, we asked whether the diatom might use a chemical signal based on the presence of a beneficial bacterium as a cue to initiate a mutualism (20). The concentration of DHPS in the *T. pseudonana* cytosol was high (3.3 mM) and similar to concentrations of compounds known to be abundant in microbial cells (21, 22), including the nitrogen homeostasis metabolite glutamate and compatible solute proline (Fig. 4). Importantly, DHPS was present in similar concentrations in the axenic and cocultured diatom cells, and present but slightly lower in B_{12} -limited diatom cells (Fig. 4). By comparison, concentrations of another ecologically important organic sulfur compound, osmolyte dimethylsulfoniopropionate (DMSP), ranged from 5 to 12 mM in cells of *T. pseudonana*, and also did not differ in the presence of bacteria. As for the bacterial side of the association, there was also no evidence of differential regulation of B_{12} pathway genes in *R. pomeroyi* DSS-3 during growth with the diatom. These findings suggest that neither of the cocultured organisms regulates biosynthesis of the currencies exchanged based on a cue linked to the physical presence of the other. They do not rule out, however, the possibility of species-specific recognition systems in naturally occurring roseobacter-diatom

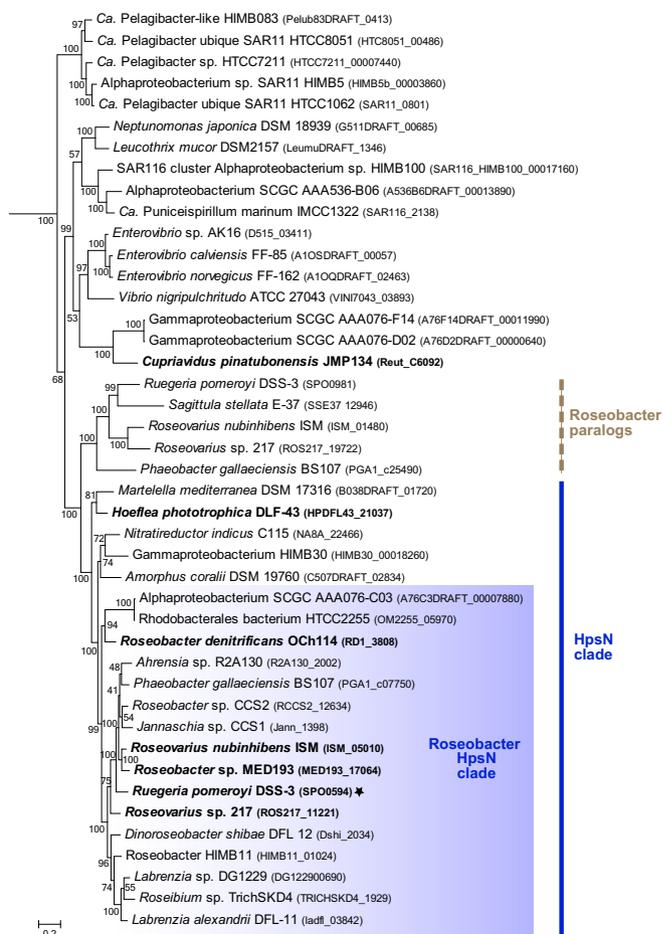


Fig. 3. A Bayesian phylogenetic tree derived from reference HpsN sequences including experimentally verified sequences (bold) and orthologs in marine genomes available through the Integrated Microbial Genomes database (img.jgi.doe.gov; see Table S3 for additional information). The tree was constructed using the P4 software following a χ^2 test on posterior distributed samples showing that a Bayesian composition-homogeneous model was adequate. Outgroups included a variety of histidinol dehydrogenase sequences. The value near each internal branch is the posterior probability, and the scale bar indicates the number of substitutions per site. Alphaproteobacterial HpsN clade sequences (and one gammaproteobacterial sequence from strain HIMB30) are marked with a bar, the clade containing Roseobacter sequences is highlighted by the purple box, and the *R. pomeroyi* DSS-3 sequence is marked with a star. HpsN paralogs in Roseobacter genomes for which function has not been determined are marked with a dashed bar. The remaining sequences are candidate HpsN proteins with varying levels of bioinformatic support. Locus tags are given in parentheses. Tree topologies based on alternate tree-building algorithms are given in Fig. S3.

associations. Alternatively, it is conceivable that these compounds do not serve as the basis of an explicit, taxonomically narrow symbiosis (23), but rather represent general metabolic linkages between broad taxonomic groups. The ubiquity of bacteria associated with the diatom phycosphere (the region surrounding the cell that is enriched in extracellular products; ref. 24) under natural conditions assures that roseobacters or other DHPS-utilizing, B_{12} -releasing bacteria will be in close proximity in the ocean.

To determine whether DHPS metabolism occurs in marine surface waters, metatranscriptomic and metabolomic data were collected from four stations along a coastal-to-open-ocean transect in the eastern North Pacific during an active diatom bloom. Counts of bacterial *hpsN* transcripts (those mapping to the Roseobacter clade with experimentally verified function; Fig. 3) reached 2.5×10^7 L⁻¹ in coastal regions of the transect

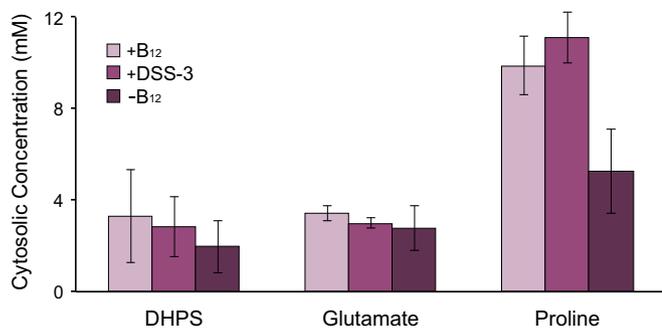


Fig. 4. Concentrations of selected metabolites in the *T. pseudonana* cytosol during exponential growth in B₁₂-replete medium (+B₁₂), in coculture with *R. pomeroyi* DSS-3 (+DSS-3), and in B₁₂-limited medium (–B₁₂), as analyzed by ultra-performance liquid chromatography mass spectrometry. Error bars represent SD of duplicate cultures.

(Station P1), decreasing 25-fold to $1.0 \times 10^6 \text{ L}^{-1}$ in the open ocean (Station P8; Fig. 5A) and tracking well with diatom cell counts. DHPS was identified in the metabolome of the eukaryotic plankton size fraction (cells $>1.6 \mu\text{m}$), where it accounted for up to 27% of a suite of major metabolites (Fig. 5B). Maximum concentrations of DHPS were similar to those of DMSP (Fig. 5C), currently considered the central metabolite of the surface ocean sulfur cycle (25) and produced primarily by dinoflagellates and haptophytes. DHPS concentration in the seawater dissolved organic matter pool was estimated to be $0.7 \pm 0.5 \text{ nM}$ ($n = 4$), consistent with efficient bacterial consumption. Given the importance of diatoms to carbon fixation in the global ocean, DHPS likely plays a major role in the flux of sulfur and carbon through marine food webs.

Biogeochemically important microbial metabolites may be cryptic because they have not yet been identified in the complex chemical milieu of seawater, or they are not readily targeted with existing analytical methods, or their concentrations are vanishingly low outside the phycosphere of phytoplankton. In waters of the eastern North Pacific, for example, chemical analysis of the organic carbon pools resolved $>7,000$ unique compounds. Unrecognized currencies in plankton interactions are highly likely to be represented among them. In this study, transcriptional responses in a two-member model organism system offered a sensitive methodology for identifying candidate metabolites of biogeochemical relevance. For DHPS, detection of this previously unrecognized diatom metabolite suggests significant new links in both the carbon and sulfur cycles that are mediated by the specific bacterial lineages capable of sulfonate catabolism.

Methods

T. pseudonana CCMP1335 was cultured in f/2 (+Si) medium at 18 °C on a 16:8 h light:dark cycle at $\sim 160 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$. *R. pomeroyi* DSS-3 cells were harvested from 1/2 YT55 medium in exponential phase and washed in f/2 medium. Four treatments were established ($n = 2$ or 4) in f/2 (+Si) medium: *T. pseudonana* +B₁₂ (369 pM), *T. pseudonana* –B₁₂, *T. pseudonana* + *R. pomeroyi*, and *R. pomeroyi* alone. For RT-qPCR, *R. pomeroyi* DSS-3 was also grown in f/2 (+Si, –B₁₂) with either acetate or DHPS. Diatom and bacterial growth was tracked by chlorophyll fluorescence and/or flow cytometry.

Cells were collected after 8 h (bacterial transcriptomics) or during exponential phase (bacterial RT-qPCR, diatom transcriptomics/metabolomics) and flash frozen in liquid N₂. RNA was extracted and processed as described (26), with slight modifications, and sequenced on either Illumina MiSeq (Illumina) or SOLiD version 4 (Life Technologies) platforms. Reads mapped using BWA (v.0.5.9) (27) were analyzed for differential expression using the baySeq package in R, with $0.2\text{--}4.4 \times 10^6$ mapped reads per sample for *R. pomeroyi* and $\sim 8 \times 10^6$ mapped reads per sample for *T. pseudonana*. RT-qPCR analysis of *hpsN* transcripts was performed as described (28). *T. pseudonana* metabolites were measured using ultra-performance liquid chromatography-high resolution mass spectrometry (UPLC-HRMS) on an Exactive Plus

Orbitrap (29) using external calibration curves generated with pure metabolite standards. These data were converted to cytosolic concentrations based on an experimentally determined fluorescence:cell number relationship and assuming a cytosolic cell volume of $30 \mu\text{m}^3$.

Experimentally verified *HpsN* sequences (11, 12) were used as queries in BLASTX analysis to identify orthologs in marine bacterial genomes. Protein sequences were aligned and trimmed, and phylogenetic trees were created assuming three different evolutionary models using the P4 and PhyloBayes software packages (30).

Marine plankton consisting primarily of eukaryotic cells (retained on a 1.6 μm or 2.0 μm pore-size filter) and seawater dissolved organic matter concentrated on solid phase extraction columns were collected in May 2012 along the North Pacific Line P transect. Analysis of cellular metabolites was carried out by liquid chromatography triple-stage quadrupole mass spectrometry (LC/TSQMS). Metatranscriptomic datasets were obtained as above, with some modifications, including addition of an internal standard to all samples immediately before cell lysis (26, 31). Reads representing *hpsN* transcripts were identified using a BLASTX search (bit score cutoff ≥ 40), and hits were confirmed by analysis of the positive reads against the RefSeq protein database. Further details of all methods are given in *SI Methods*.

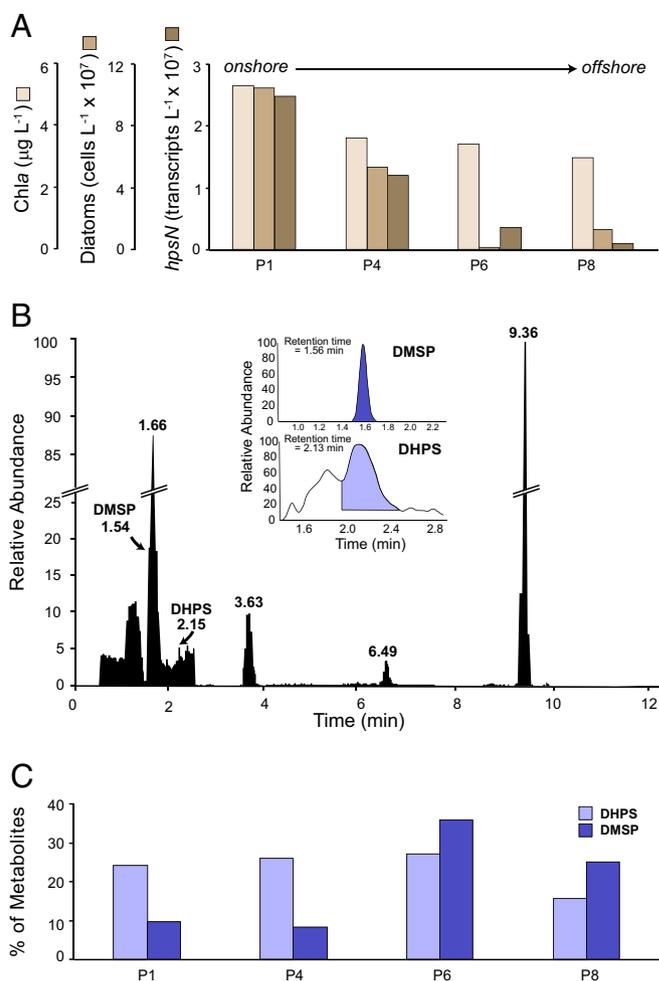


Fig. 5. DHPS cycling in the eastern North Pacific Ocean. (A) Chlorophyll a concentrations, diatom counts, and Roseobacter-clade *hpsN* transcript abundance at four stations along the Line P transect. (B) Total ion current chromatogram for the Station P4 sample collected by triple-stage quadrupole mass spectrometry, with insets showing DHPS and DMSP peak details. R^2 values of standard curves with authentic standards were 0.98 for both compounds. Other identified compounds include glycine betaine (1.66 min; coeluting with additional small organic acids), phenylalanine (3.63 min), a mixture of thymidine and 5-methylthioadenosine (6.49 min), and the deuterated biotin injection standard (9.36 min; coeluting with lesser amounts of riboflavin and biotin). (C) DHPS and DMSP concentrations as a percent (by mass) of 30 measured metabolites in the eukaryotic plankton size fraction ($>1.6 \mu\text{m}$ diameter) at four Line P stations.

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