Stimulation of gross dimethylsulfide (DMS) production by solar radiation

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[1] Oceanic gross DMS production (GP) exerts a fundamental control on the concentration and the sea-air flux of this climatically-active trace gas. However, it is a poorly constrained process, owing to the complexity of the microbial food web processes involved and their interplay with physical forcing, particularly with solar radiation. The “inhibitor method”, using dimethylsulphide (DMDS) or other compounds to inhibit bacterial DMS consumption, has been frequently used to determine GP in dark incubations. In the work presented here, DMDS addition was optimized for its use in light incubations. By comparing simultaneous dark and light measurements of GP in mesotrophic ultraoligotrophic waters, we found a significant enhancement of GP in natural sunlight in 7 out of 10 experiments. Such stimulation, which was generally between 30 and 80% on a daily basis, occurred throughout contrasting microbial communities and oceanographic settings. Citation: Galí, M., V. Saló, R. Almeda, A. Calbet, and R. Simó (2011), Stimulation of gross dimethylsulphide (DMS) production by solar radiation, Geophys. Res. Lett., 38, L15612, doi:10.1029/2011GL048051.

1. Introduction

[2] Oceanic DMS is a minor volatile byproduct of the microbial cycling of dimethylsulfiniopropionate (DMSP), a multifunctional osmolyte produced by ubiquitous oceanic phytoplankton [Simó, 2001; Stefels et al., 2007]. Even though only a tiny fraction (generally <10%) eventually escapes to the atmosphere, its global emission amounts ca. 28 Tg S yr−1 [Lana et al., 2011], and comprises >90% of the biogenic sulfur flux and around 20% of the total (man-made, volcanic and biogenic) sulfur flux to the atmosphere [Simó, 2001]. Several DMS(P) cycling processes are influenced by solar radiation. This translates into a positive correlation between solar radiation and DMS concentration in most of the surface ocean, across latitudes and seasons [Vallina and Simó, 2007]. This correlation provides support for the controversial CLAW hypothesis [Charlson et al., 1987], which postulates that a negative feedback between oceanic plankton and the radiative forcing could occur through the influence of DMS emissions on atmospheric aerosol chemistry and, ultimately, on the albedo of stratus-form clouds.

[3] The major DMS removal pathways in the upper mixed layer (UML) are photolysis and bacterial consumption, and their response to sunlight is relatively well understood [Toole et al., 2006]. In contrast, DMS production mechanisms and their response to physical forcing are more poorly known. Microbial processes contributing to DMS production include phytoplankton release upon enzymatic cleavage of DMSP, phytoplankton autolysis, non-assimilatory microbial DMSPd metabolism, and viral lysis and zooplankton grazing on DMS producers [Stefels et al., 2007]. With current methods, the contribution of each process to bulk GP cannot be determined independently. Moreover, it could well be that the sum of the different components did not yield the actual GP rates due to unexpected interactions. Hence, DMS cycling studies have to rely on determinations of bulk GP rates.

[4] Two distinct approaches, with their own advantages and pitfalls, exist for the determination of GP: a direct measurement, generally by use of bacterial consumption inhibitors in dark incubations [Simó et al., 2000; Wolfe and Kiene, 1993]; or an indirect estimate, which requires determining the bulk net DMS evolution over time together with all the consumption terms [Bailey et al., 2008]. The latter approach can benefit from accurate radioisotope measurements of DMS loss rates, but suffers from increased uncertainty owing to error propagation, since at least three rate measurements are involved in the budget. In addition, radiolabeled DMS (e.g., 35S-DMS) is not commercially available. On the other hand, the inhibitor method, though allowing direct determination of GP, is dependent on the efficiency of the inhibitor used and, if applied under natural light conditions, requires the simultaneous measurement of the photochemical DMS loss, which also contributes error. In this work we present evidence of increased GP (as determined with the inhibitor method) due to sunlight exposure and propose alternative hypotheses to explain this observation.

2. Methods

2.1. Sampling and Oceanographic Data Processing

[5] Six different months throughout the seasonal cycle were sampled in the coastal NW Mediterranean, whereas the Southern Indian Ocean Subtropical Gyre and the Tasman Sea were sampled during the austral summer aboard the R/V Hespérides (Table 1). Vertical profiles of conductivity, temperature and photosynthetically active radiation (PAR) were obtained from CTD casts, and subsequently processed to calculate the mixed layer depth (MLD) and the diffuse attenuation coefficient of downwelling PAR (Kd,PAR). Total solar irradiance of the prior 48 h, recorded by land- or ship-based meteorological stations, was used for light history calculations. Depending on the water column stability, the previous exposure of microbial communities to solar radiation (SRUML) was calculated as the UML average [Vallina 

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and Simó, 2007] or as that found at the sampling depth (see auxiliary material).\(^1\) Surface water samples (5 or 3 m depth) were collected in the morning and incubated on a building’s roof (Mediterranean) or on the ship’s deck (Indian Ocean and Tasman Sea) as described below. Further details about the procedures concerning ancillary data reported herein are given by Calbet et al. [2008].

### 2.2. Incubations and DMS(P) Analyses

[\(\text{SR}_{\text{UNL}}\) and \(\text{SR}_{\text{EXP}}\), respectively, stand for in situ and experimental exposure to solar radiation. Abbreviated phytoplankton group names are: Diat (diatoms); Crypt (cryptophytes); Hapt (haptophytes, or prymnesiophytes); Dino (dinoflagellates); Syn (Synechococcus); Pro (Prochlorococcus); Neuk (neoukaryotes); Peak (picoukaryotes). Neuk and Peak are populations defined by flow cytometry, with no taxonomic meaning a priori.]

#### Table 1. Summary of Characteristics of the Initial Water Samples

<table>
<thead>
<tr>
<th>Date</th>
<th>Lat.(^{\circ})N</th>
<th>Long.(^{\circ})E</th>
<th>Temp. (°C)</th>
<th>MLD (m)</th>
<th>(\text{SR}_{\text{UNL}}) (W m(^{-2}))</th>
<th>(\text{SR}_{\text{EXP}}) (W m(^{-2}))</th>
<th>Chl (a) (µg L(^{-1}))</th>
<th>Chl (a) &lt;10 µm (%)</th>
<th>Dominant Phyto</th>
<th>DMS (nmol L(^{-1}))</th>
<th>DMS(\text{P}) (nmol L(^{-1}))</th>
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</thead>
<tbody>
<tr>
<td>Mediterranean (Coastal Station)</td>
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</tr>
<tr>
<td>11/29/05</td>
<td>41.22</td>
<td>2.13</td>
<td>16.1</td>
<td>40</td>
<td>14</td>
<td>61</td>
<td>0.97</td>
<td>61</td>
<td>Diat &gt;&gt; Crypt &gt; Hapt</td>
<td>1.5</td>
<td>11.4</td>
</tr>
<tr>
<td>01/18/06</td>
<td>41.22</td>
<td>2.13</td>
<td>13.0</td>
<td>40</td>
<td>13</td>
<td>47</td>
<td>0.47</td>
<td>81</td>
<td>Crypt &gt;&gt; Diat &gt; Hapt</td>
<td>0.91</td>
<td>12.4</td>
</tr>
<tr>
<td>05/16/06</td>
<td>41.22</td>
<td>2.13</td>
<td>18.1</td>
<td>5</td>
<td>116</td>
<td>176</td>
<td>0.95</td>
<td>60</td>
<td>Diat &gt;&gt; Hapt &gt;&gt; Crypt</td>
<td>1.6</td>
<td>10.0</td>
</tr>
<tr>
<td>06/14/06</td>
<td>41.22</td>
<td>2.13</td>
<td>21.1</td>
<td>5</td>
<td>155</td>
<td>178</td>
<td>0.49</td>
<td>88</td>
<td>Dino &gt; Hapt &gt;&gt; Crypt</td>
<td>7.8</td>
<td>71.0</td>
</tr>
<tr>
<td>07/31/06</td>
<td>41.22</td>
<td>2.13</td>
<td>24.4</td>
<td>nd</td>
<td>183</td>
<td>182</td>
<td>0.39</td>
<td>79</td>
<td>Diat &gt;&gt; Sync &gt;&gt; Crypt</td>
<td>5.2</td>
<td>17.5</td>
</tr>
<tr>
<td>08/29/06</td>
<td>41.22</td>
<td>2.13</td>
<td>24.4</td>
<td>nd</td>
<td>118</td>
<td>92</td>
<td>0.31</td>
<td>90</td>
<td>Sync &gt; Hapt &gt;&gt; Crypt</td>
<td>5.7</td>
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</tr>
<tr>
<td>Indian Ocean and Tasman Sea</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Chl (a) &lt;2 µm</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>02/24/11</td>
<td>–30.05</td>
<td>61.46</td>
<td>24.9</td>
<td>32</td>
<td>103</td>
<td>124</td>
<td>0.094</td>
<td>63</td>
<td>Pro &gt;&gt; Neuk &gt; Peak</td>
<td>0.73</td>
<td>6.8</td>
</tr>
<tr>
<td>02/28/11</td>
<td>–29.56</td>
<td>72.45</td>
<td>24.5</td>
<td>31</td>
<td>129</td>
<td>86</td>
<td>0.040</td>
<td>46</td>
<td>Neuk &gt;&gt; Pro &gt; Peak</td>
<td>1.04</td>
<td>7.4</td>
</tr>
<tr>
<td>02/04/11</td>
<td>–29.75</td>
<td>86.26</td>
<td>22.5</td>
<td>26</td>
<td>230</td>
<td>225</td>
<td>0.033</td>
<td>51</td>
<td>Pro &gt;&gt; Neuk &gt; Peak</td>
<td>0.96</td>
<td>7.5</td>
</tr>
<tr>
<td>03/28/11</td>
<td>–38.66</td>
<td>150.42</td>
<td>21.1</td>
<td>46</td>
<td>54</td>
<td>70</td>
<td>0.34</td>
<td>73</td>
<td>Pro &gt;&gt; Sync &gt; Peak</td>
<td>0.78</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Although DMS evolution with intermediate time points was monitored during all dark incubations (as well as in light incubations, though with lower frequency), we calculated \(GP_D\) with the \(t_f - t_0\) approach for coherence with \(aGP_L\). \(GP_D\) rates calculated in this manner differed from regression-derived \(GP_D\) by a 0 – 27% (mean 9%) excess (see auxiliary material).

### 2.3. Photolysis Correction and DMS Photolysis in DMDS-Amended Incubations

[\(\text{SR}_{\text{UNL}}\) and \(\text{SR}_{\text{EXP}}\), respectively, stand for in situ and experimental exposure to solar radiation. Abbreviated phytoplankton group names are: Diat (diatoms); Crypt (cryptophytes); Hapt (haptophytes, or prymnesiophytes); Dino (dinoflagellates); Syn (Synechococcus); Pro (Prochlorococcus); Neuk (neoukaryotes); Peak (picoukaryotes). Neuk and Peak are populations defined by flow cytometry, with no taxonomic meaning a priori.]

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\[K_{\text{photo,inc}} = -\ln \left( \frac{[\text{DMS}]_f}{[\text{DMS}]_0} \right) / (t_f - t_0) \tag{2}\]

where \([\text{DMS}]_f\) and \([\text{DMS}]_0\) are, respectively, the final \([\text{DMS}]\) (after being corrected for dark DMS production in filtered waters) and initial \([\text{DMS}]\). The mean DMS photolysis rate \((\langle \text{Photo} \rangle_{\text{inc}})\) was computed from mean \([\text{DMS}]\) during the incubation \(([\text{DMS}]_{\text{inc}})\), defined as the average of \([\text{DMS}]_f\) and \([\text{DMS}]_0\):

\[\langle \text{Photo} \rangle_{\text{inc}} = K_{\text{photo,inc}} \langle [\text{DMS}] \rangle_{\text{inc}} \tag{3}\]

and \(aGP_L\) was corrected following:

\[GP_L = aGP_L + \langle \text{Photo} \rangle_{\text{inc}} \tag{4}\]

In addition to the simple correction, we also calculated a time-resolved photolysis that accounted for nonlinearity due to the first-order kinetics of DMS photolysis and the diel variation in irradiance. Only very small differences between the two methods were observed (smaller than the experimental error), so we used the simple correction outlined in equations (2) to (4) throughout.

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\(^1\)Auxiliary materials are available in the HTML. doi:10.1029/2011GL048051.
The concern arose as to whether DMDS addition to whole water bottles interferes with the kinetics of DMS photolysis. To test this, we performed a series of independent DMS photochemistry experiments, where <0.2 \( \mu \text{mol L}^{-1} \) filtered (or <30 kDa tangential flow filtered) seawater was spiked with DMDS at concentrations ranging from 100 nmol L\(^{-1}\) to 2 \( \mu \text{mol L}^{-1}\). No significant effects (compared to unamended samples) were observed at [DMDS] less than or equal to 200 nmol L\(^{-1}\). Above this concentration, DMDS caused an increase in DMS photolysis and the departure from first-order kinetics (Figure 1). Since DMDS does not appreciably absorb actinic radiation, its effect could happen through a concentration-dependent transient increase in the amount of oxidants. Therefore, a maximum [DMDS] of 200 nmol L\(^{-1}\) is recommended to avoid underestimation of \( GP_L \).

3. Results and Discussion

[10] Our study covered a wide range of environmental conditions, evident in the water column stratification parameters, phytoplankton biomass and community composition summarized in Table 1. In terms of sulfur cycling, this is illustrated by the extremely wide range displayed by the DMSP/Chl\(_b\) ratio (12 – 227 nmol \( \mu \text{g}^{-1}\)). In Mediterranean samples, low \( GP_D \) rates were found in the vertically mixed waters of November and January (<1 nmol L\(^{-1}\) d\(^{-1}\)), whereas the stratified waters of May through August displayed higher \( GP_D \) rates (2.3–6.3 nmol L\(^{-1}\) d\(^{-1}\)). This resembles the seasonal pattern of \( GP_D \) found by Vila-Costa et al. [2008] at the nearby Blanes Bay Microbial Observatory. In the Indian Ocean and Tasman Sea, dark \( GP_D \) rates ranged 0.38 – 0.82 nmol L\(^{-1}\) d\(^{-1}\), in accordance with the low plankton biomass and DMSP\(_t\) concentrations found.

[11] Once corrected for photochemical DMS loss, \( GP_L \) was significantly higher than \( GP_D \) in 7 out of 10 experiments (‘significant’ meaning that their respective error intervals – the ranges of duplicate incubations – did not overlap; Figure 2). The January sample was the most responsive, with a 207% difference between \( GP_L \) and \( GP_D \), coinciding with a severe experimental overexposure (Table 1). The remaining 6 samples where significant stimulation occurred, which were exposed to more realistic irradiance, displayed stimulations between 30 and 78%. On the other hand, two of the samples displaying no significant stimulation were clearly underexposed during the incubations (Aug and Ind2). Yet, no significant correlation could be found between sunlight-stimulated \( GP \) and light history, experimental exposure, or any other biotic or abiotic variable.

[12] Support for light-stimulated gross DMS production exists in the experimental literature. However, no attempts have been made at constraining its magnitude on a daily basis, a key time frame for DMS cycling studies. In the Sargasso Sea, Toole et al. [2006] observed that total DMS loss (as measured with \( ^{35}\text{S}-\text{DMS} \)) increased at higher irra-

![Figure 1](image1.png)

**Figure 1.** Effects of DMDS additions on DMS photolysis. Different symbols and fillings in the legend denote different DMDS concentrations added, in \( \mu \text{mol L}^{-1}\). Letters in parentheses denote the different samples incubated (only time-course experiments shown; see auxiliary material for additional experiments). The equations fitted are Michaelis-Menten-like curves or straight lines. Initial DMS concentrations (nmol L\(^{-1}\)) are: 21.1 (B); 27.8 (C); and 9.1 (D).

![Figure 2](image2.png)

**Figure 2.** Gross DMS production obtained in the dark (\( GP_D \)) and light (\( GP_L \)) incubations, calculated from initial and final DMS concentrations, and associated uncertainty. Grey intervals on white bars represent \( aGP_L \pm \text{error range} \), so that the relative weight of the photolysis correction on the final \( GP_L \) values can be appreciated. Stars denote experiments where the error ranges of \( GP_D \) and \( GP_L \) did not overlap.
diances and higher proportions of shortwave UVR mainly due to increased photochemical loss. Nevertheless, net DMS production remained very close to zero irrespective of UVR dose, indicating that an extra source of DMS must exist to compensate for the increased loss. These results also indicated some spectral dependence of DMS production, which deserves further investigation.

[13] Stress-induced DMS release by phytoplankton is feasible based on physiology. In this regard, two nonexclusive explanations have been put forward relating it with high irradiance and nutrient starvation: the overflow hypothesis [Stefels, 2000] by which DMSP and DMS serve as an overflow mechanism when phytoplankton undergo unbalanced growth; and the antioxidant hypothesis [Sunda et al., 2002], which states that the downstream products of DMSP cleavage, including DMS, could act as intracellular radical scavengers. Cell membrane-permeating DMS would leak from this protective cascade of antioxidant metabolites. DMS + DMSP release rates of the order of 1 to 11% d⁻¹ (as % of the intracellular DMSP pool) have been reported for axenic cultures of haptophyte and dinoflagellate strains [Stefels et al., 2007]. Remarkably, Archer et al. [2010] recently found higher values during short term exposure to UV of a non-axenic Emiliania huxleyi strain: 8–14% d⁻¹ for DMS and 13–22% d⁻¹ for DMSP, which could supply a considerable fraction of the sunlight-induced GP.

[14] In the field, and consistent with both the overflow and the antioxidant hypotheses, potential enzymatic DMSP to DMS conversion (the so-called “lyase” activity) has been shown to correlate with radiative stress conditions [Bell et al., 2007; Harada et al., 2004]. However, the relative importance of sublethal physiological responses (like the up-regulation of DMSP synthesis and/or lyase activity) compared to lethal UV damage of the most sensitive phytoplankton [Agustí and Llabrés, 2007] is unknown. UVR-induced cell membrane damage or, directly, cell disputation, would induce DMSP release, along with algal lysates from some phytoplankton, stimulating DMS production without any need for short-term physiological regulation.

[15] But, is algal release the major driving mechanism behind sunlight-induced DMS production? UVR seems to enhance DMSP exudation, and a variable fraction of the dissolved DMSP (DMSPD) pool will be channelled to DMS depending on the dissolved lyase activity, the yield of dissolved DMSPD to DMS conversion by bacteria, and the algal share of DMSPD uptake [Vila-Costa et al., 2006]. Enhancement of the bacterial yield by UVR has been proposed, but Slezak et al. [2007] obtained inconclusive results: bacterial yields did not always increase after irradiation, and when they did, they were often offset by severe photoinhibition of bacterial DMSPD uptake. Even more uncertain are the interactive effects of UVR exposure and food-web processes like viral lysis and microzooplankton grazing [Sommaruga, 2003], but they should not be overlooked. Microzooplankton grazing accounted for 63 and 72% of GPₓ in our experiments of June and July, respectively [Saló et al., 2010].

[16] The existence of a sunlight-associated DMS source is also consistent with mechanistic and diagnostic models. At low latitudes, annual maxima of DMS concentrations co-occur with the lowest plankton biomass, a feature named the “summer DMS paradox” [Simó and Pedrós-Alió, 1999]. Reproducing this uncoupling represents a challenge for modelers [Le Clainche et al., 2010], and some recent studies [Toole et al., 2008; Vallina et al., 2008; Vogt et al., 2010] have identified stress-induced (algal) DMS release as the key mechanism allowing mechanistic models to simulate the summer paradox.

[17] At the global scale, marine ecosystems are facing important changes in the decades to come. UVR-transparent, highly irradiated oligotrophic waters are expanding due to global warming and increased vertical stratification [Polovina et al., 2008], thus expanding the “stress regime” areas, as depicted by Toole and Siegel [2004]. Conversely, diagnostic modeling exercises suggest that DMS emission is a very resilient ecosystem function, which should undergo very little fluctuations in the near future in spite of enhanced stratification due to global warming [Vallina et al., 2007]. Our work points at sunlight as an important modulator of DMS production, but further work is required to understand the physiological and ecological basis of sunlight-driven DMS production and its variability across dier to seasonal time scales.

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References


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