Aquatic Botany 90 (2009) 37–42

Contents lists available at ScienceDirect

Aquatic Botany

journal homepage: www.elsevier.com/locate/aquabot

Effects of UV radiation and nitrate limitation on the production of biogenic sulfur compounds by marine phytoplankton

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ARTICLE INFO

Article history:
Received 12 January 2007
Received in revised form 18 May 2008
Accepted 20 May 2008
Available online 21 July 2008

Keywords:
Oxidative stress
Antioxidant
Amphidinium carterae
Thalassiosira oceanica

ABSTRACT

We tested the effects of UV radiation (UVR) and nitrate limitation on the production of dimethylsulfide (DMS), particulate dimethylsulfoniopropionate (DMSPp), and particulate dimethylsulfoxide (DMSOp) in natural seawater from the Gulf of Mexico and in phytoplankton cultures. DMS/Chl *a* ratios in PAR-only and PAR + UV-exposed seawater were 0.44–2.0 and 0.46–1.9 nmol DMS μg^{-1} Chl *a*, respectively, whereas the ratios in cultures of *Amphidinium carterae* were 1.0–2.2 nmol μg^{-1} in PAR-exposed samples and 0.91–2.1 nmol μg^{-1} in PAR + UV-exposed samples. These results suggested that UVR did not substantially affect DMS/Chl *a* ratios in seawater and *A. carterae* culture samples. Similarly, UVR had no significant effect on DMSOp/Chl *a* in seawater samples (0.83–1.6 nmol DMSO μg^{-1} Chl *a* for PAR + UV vs. 0.70–1.5 nmol μg^{-1} for PAR-exposed seawater samples, respectively) or in *A. carterae* cultures (0.20–1.3 and 0.19–0.88 nmol DMSO μg^{-1} Chl *a* in PAR + UV- and PAR-exposed cultures, respectively). In an experiment with the diatom, *Thalassiosira oceanica*, the culture was grown in high nitrate (30 μM) or low nitrate (6 μM) media and exposed to PAR-only or PAR + UV. The low nitrate, PAR-only samples showed an increase of intracellular dimethylsulfoniopropionate (DMSP) concentration from 2.1 to 15 mmol L^{-1} in 60 h, but the increase occurred only after cultures reached the stationary phase. Cultures of *T. oceanica* grown under UVR had lower growth rates than those under PAR-only ($\mu' = 0.17$ and 0.32 d^{-1}, respectively) and perhaps did not experience severe nitrate limitation even in the low nitrate treatment. These results suggest that the elevated UVR in low nitrate environments could result in reduction of DMSP in some species, whereas DMSP concentrations would not be affected in eutrophic areas.

1. Introduction

Dimethylsulfoniopropionate (DMSP) is a solute commonly found in several classes of marine phytoplankton, such as diatoms, dinoflagellates and prymnesiophytes (Keller and Korjeff-Bellows, 1996). Some bacteria and phytoplankton are able to cleave DMSP enzymatically into dimethylsulfide (DMS) (Stefels and Van Boekel, 1993; Todd et al., 2007). DMS is a volatile organic sulfur compound that contributes approximately 50% of the global biological sulfur flux to the atmosphere (Bates et al., 1992). Once in the atmosphere, DMS is oxidized to form sulfate aerosols, which act as cloud-condensation nuclei potentially affecting global climate (Bates et al., 1987; Charlson et al., 1987).

Another sulfur compound found in phytoplankton and seawater is dimethylsulfoxide (DMSO) (Simó et al., 1998). Potential sources of DMSO include photo-oxidation of DMS and hydroxyl radical ($OH^{\bullet}$) reaction with DMS, DMSP or any of its precursors (Lee and de Mora, 1999; Sunda et al., 2002). These reactions can occur in natural water as well as in phytoplankton cells. DMSO is permeable to biological membranes, yet particle-associated DMSO concentrations were higher than those of dissolved DMSO in seawater and phytoplankton cultures (Simó et al., 1998). Therefore, DMSO is likely produced in biological cells.

Because of its high intracellular concentrations in some phytoplankton species (up to several hundred mM), DMSP may function as an osmolyte as well as cryoprotectant (Karsten et al., 1996). Lee and de Mora (1999) also suggested potential roles of DMSO as cryoprotectant and osmoregulator. Previous studies have, however, reported that the intracellular accumulation of DMSP plays a minor role in short-term osmoregulation (Kirst, 1996), and DMSP and DMSO variability in the ocean, where salinity is stable, cannot be explained by osmoregulation. In addition, cryoprotection is not necessary for species that produce DMSP and DMSO in mid- to low-latitudes. Therefore, DMSP and DMSO are likely to have functions other than osmolyte and cryoprotectant.

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doi:10.1016/j.aquabot.2008.05.004

Previous studies have shown that DMSP and DMS concentrations in a broad range of subtropical, temperate and subarctic oceanic waters are high under stratified conditions during late spring to early fall and low during winter (Dacey et al., 1998; Simó and Pedrós-Alió, 1999). In addition, the ratios of DMSP and DMS to Chl *a* are normally highest near the surface and tend to decrease with depth (Belviso et al., 1993; Simó et al., 1995; Dacey et al., 1998). These observations suggest that the production of DMSP and related compounds may be related to high irradiation or nutrient limitation. Such conditions can elevate oxidative stress in marine organisms, and Sunda et al. (2002) suggested that DMSP and its enzymatic breakdown products, DMS and acrylate, may protect phytoplankton from reactive oxygen species (ROS), particularly highly reactive hydroxyl radicals.

UV radiation is one form of stress that enhances the production of ROS inside and outside of organisms. For example, UV radiation inhibited the electron transport and decreased the maximum quantum yield of photosystem II (Fv/Fm) (Marwood et al., 2000) and reduced the growth rate and increased the cell volume of *Emiliania huxleyi* (Garde and Cailiau, 2000).

Nutrient limitation causes metabolic imbalances, which lead to elevated levels of oxidative stress (Bucciarelli and Sunda, 2003). Under oxidative stress, primary producers increase the production of antioxidants and antioxidant enzymes (Lesser and Shick, 1989). However, antioxidant enzymes and some antioxidants require nitrogen. Because DMSP and its enzymatically cleaved products have high rate constants with hydroxyl radicals, phytoplankton may produce DMSP as N-free antioxidants under nitrogen limitation (Sunda et al., 2002; Bucciarelli and Sunda, 2003).

UV radiation (UVR), nitrate limitation, or the combination of these factors may affect the concentration of the methylated sulfur compounds due to elevated oxidative stress. The present study tested the effects of UVR on the concentrations of DMS, particulate DMSP (DMSPp) and particulate DMSO (DMSOp) in coastal water from the Gulf of Mexico and in two cultured species of phytoplankton: the dinoflagellate, *Amphidinium carterae* and the diatom, *Thalassiosira oceanica*. These species are known to produce DMSP, and they are commonly found in seawater. In addition, the effects of UVR combined with high and low nitrate conditions were tested on the diatom, *T. oceanica*.

2. Methods

2.1. Experimental conditions

2.1.1. Effects of UV radiation on natural water

Water from the coastal Gulf of Mexico was collected on July 10, 2001 from the public-beach pier on Dauphin Island, AL (30°14′50″N and 88°07′33″W). The water was filtered through a 200-μm mesh net to exclude large zooplankton and put into six FEP Teflon bottles (1 L; Nalgene). Two bottles were used for zero time measurements. The other four bottles were placed in an outdoor incubator with flow-through water to maintain ambient temperature. Two bottles were placed under a UF-3 panel which blocked UV radiation but allowed PAR transmission. The incubator was covered with a black mesh, which blocked approximately 50% of the incident solar radiation, to approximate ambient light intensity at the collection site. Aliquots of water from each bottle were taken at each sampling time for measurements of Chl *a*, DMS, DMSPp, and DMSOp concentrations. Sampling times were 07:00, 13:00 and 20:00 h for the first 2 d and 13:00 h on the third and fourth days. We sampled three times a day for the first 2 d to observe the short-term response to UV and no-UV exposure. Only the measurements at 13:00 h were used for the statistical analysis to maintain the 24-h sampling interval and avoid bias due to changes in irradiance.

2.1.2. Effects of UV radiation on the dinoflagellate A. carterae

A. carterae was grown in F/4 medium (Guillard, 1975) in a temperature-controlled room equipped with UV light (UV-A 340 Lamp; Q-Panel Co.) and cool-white fluorescent lights. The cultures were placed in four acid-washed, UV-transparent Ziploc bags and all bags were exposed to fluorescent light from 08:00 to 20:00 h. Two of the bags were exposed to UV lights from 10:00 to 16:00 h, and the other two were protected from UV by covering with a UF-3 panel. Samples were taken at 08:00 h (end of dark period) and at 16:00 h (end of UV period) for 84 h and analyzed for DMS, DMSPp, DMSOp and Chl *a* concentrations. The light intensity of UV-A was 0.865 mW cm^{-2}, UV-B was 0.155 mW cm^{-2} and the total irradiance was 450 μmol photon μm^{-2} s^{-1} (approximately 50% higher UV:PAR than natural radiation, based on measurements taken when the sun is at the zenith at Dauphin Island, AL, latitude 30°14′50″N in May). Since UV light was turned on only for 6 h of 12-h photoperiod to imitate changes in natural UV radiation, the daily UV:PAR was approximately 25% higher than the natural solar radiation. The UV-A 340 lamp had very similar spectral characteristics to natural UV radiation from the solar cutoff point of 295–365 nm. Only the measurements at 16:00 h were used for the statistical analysis to maintain the 24-h sampling interval and avoid bias due to changes in irradiance.

2.1.3. Effects of UV and nitrate limitation on the diatom, T. oceanica

An axenic culture of *T. oceanica* (CCMP1005) was grown in four Teflon bottles with 30 μM nitrate (high nitrate treatment, equivalent to F/58.8) and four Teflon bottles with 6 μM nitrate (low nitrate treatment). Other nutrient concentrations in the 6 μM nitrate treatment were the same as in the 30 μM treatment (i.e. F/58.8 levels). The culture media were prepared in 0.2 μm-filtered oligotrophic Sargasso Sea water collected in August 2004. Thus, the nutrients in the stock seawater did not affect the final concentration of the media. The cultures were placed in an incubator equipped with UV light (UV-A 340 Lamp; Q-Panel Co.) and fluorescent lights. The light cycle was 12-h photoperiod and the mean irradiance for PAR was 600 μmol photon m^{-2} s^{-1}. UV-A and UV-B intensities were 0.34 and 0.06 mW cm^{-2}, respectively (15% higher UV:PAR than natural radiation measured when the sun is at the zenith at Dauphin Island, AL, latitude 30°14′50″N in May). Semi-continuous cultures were maintained for 3 d with UV and without UV, and then batch cultures were started at T_0. Two bottles each of high nitrate and low nitrate samples were placed in a UV opaque box within the incubator and the other four bottles were placed directly in the incubator and exposed to UV. Aliquots of cultures were taken for measurements at the end of the dark and light periods for 3 d. We did not measure DMS for this culture because *T. oceanica* did not have detectable DMSP lyase activity to produce DMS. Unfortunately, we had to discard the DMSO samples from this experiment because a stock of NaOH used in the analysis procedure became contaminated with DMSO. Only the measurements at the end of light periods were used for the statistical analysis to maintain the 24-h sampling interval and avoid bias due to irradiance.

2.2. Sulfur compound measurement

Concentrations of DMS in samples were measured with the purge and trap technique as described in Kiene and Service (1991). For DMSPp and DMSOp, 50 mL subsamples of natural water, 2 mL of *A. carterae* culture, and 10 mL of *T. oceanica* culture were filtered by gravity onto glass-fiber filters and the filters were placed immediately into a 14-mL serum vials and then sealed with a Teflon-coated gray butyl stoppers. The concentrations of DMSPp and DMSOp in each sample were measured sequentially. First,

DMSPp was converted to DMS by adding 1 mL of 5 N NaOH to the vials. The vials were incubated in the dark at room temperature, approximately 25 °C, for at least 12 h to complete the reaction, then small headspace sub-samples were withdrawn from the vials with a gastight syringe and inject into a gas chromatograph (Shimadzu GC-14 A). After the DMSPp measurements, the vials were purged with N_2 gas to remove DMS. An equal volume of HCl (6 N) to NaOH was added to the vials to neutralize the samples, and the same volume of $TiCl_3$ (20% (wt/v) stabilized solution; Fisher Scientific) was added to the vials to convert DMSOp to DMS (Kiene and Gerard, 1994). The vials were incubated at 50 °C in a water bath for 2 h to complete the reaction. After the vials were cooled to room temperature, a headspace sub-sample was injected into the gas chromatograph and the DMS produced from DMSO was quantified.

2.3. Biomass estimate and Fv/Fm measurements

Chl *a* was measured by the non-acidification method, described by Welschmeyer (1994). Sample water was filtered onto a glass-fiber filter and the filter was placed in a centrifuge tube with 10 mL 90% v/v HPLC grade acetone. The tubes were kept in a freezer for 24 h after which the Chl *a* concentration was measured with a fluorometer (Turner Designs TD-700). For *T. oceanica* samples, cell abundance and cell volume were measured with a Multisizer™ 3 Coulter Counter® (Beckman Coulter, Inc.). The maximum quantum yield of photosystem II (Fv/Fm) was measured with a Water PAM fluorometer (Heinz Walz GmbH). Relative growth rate (μ') in $Log_{10}\ d^{-1}$ was calculated for the exponential growth phase based on cell volume (Fogg and Thake, 1987).

2.4. Statistics

Two-way repeated-measures ANOVA was used to analyze the Gulf of Mexico water and *A. carterae* experiments, and three-way repeated-measures ANOVA was used to analyze the *T. oceanica* data. Light (PAR + UV and PAR-only) and nitrate (high and low nitrate concentration) were the between-subject factors, and time was the within-subject factor. In some instances, the condition of equality of variances (i.e. homocedasticity) was not met. However, it is well accepted that ANOVA is robust to most violations of homocedasticity (Sokal and Rohlf, 1995; Zar, 1998), and thus, we decided to use repeated-measures ANOVA in all our experiments after setting the significance level (α) at <0.01 to correct for the higher chance of incurring a type I error (i.e. rejecting a true null hypothesis) when that violation is committed. The Greenhouse-Geisser Epsilon correction, following the recommendations of Maxwell and Delaney (1990), was used when the condition of sphericity was not met. Statistical analyses were performed with Systat 11.0 and Sigmastat 3.0.

3. Results

3.1.1. Gulf of Mexico coastal water

During the outdoor incubation, Chl *a* concentrations gradually decreased from 5.9 to 1.8 $\mu g\ L^{-1}$ in 4 d ($P = 0.006$), and the concentrations were nearly identical between PAR + UV and PAR-only treatments after 79 h (Fig. 1a). DMS concentration varied between 2.6 and 6.9 $nmol\ L^{-1}$ for PAR-only samples and 2.7 and 5.0 $nmol\ L^{-1}$ for PAR + UV samples (Fig. 1b). Chl *a*-normalized DMS, DMSPp and DMSOp are used to estimate concentrations of these chemicals per biomass. Chl *a*-normalized DMS concentration increased from 0.44 to as high as 2.0 $nmol\ \mu g^{-1}$ under PAR + UV exposure, and overall DMS/Chl *a* increased with time ($P = 0.019$). There was a difference between PAR + UV and PAR-only treatments with respect to DMS/Chl *a* ($P = 0.05$). UV exposure resulted in higher DMS/Chl *a* during the first 38 h, and DMS/Chl *a* was nearly identical on days 3 and 4 between the two treatments (Fig. 1c). DMSPp/Chl *a* increased with time ($P = 0.001$; Fig. 1d). However,

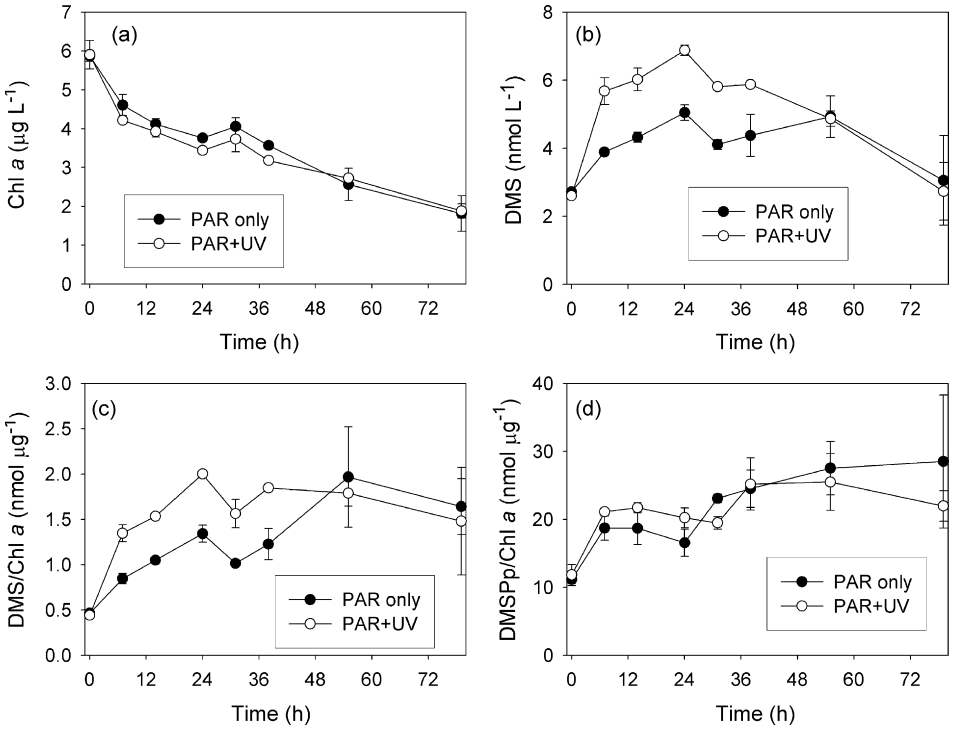

Fig. 1. Effects of UVR on Chl *a* (a) and DMS concentrations (b), Chl *a*-normalized DMS (c) and DMSPp (d) in water sample collected from the coastal Gulf of Mexico. The water samples were incubated in sunlight and UVR was removed by incubation under UV-opaque UF-3 acrylic panel. Overall light intensity was reduced by 50% for all samples by incubation under neutral density screening.

there were no significant differences between UV and non-UV treatments for DMSPp/Chl *a*, as well as DMSOp/Chl *a* ($P = 0.164$ and $P = 0.966$, respectively). DMSOp/Chl *a* varied between 0.8 and 1.6 nmol DMSO μg^{-1} Chl *a*, but there was no differences between UV and non-UV treatments for the DMSOp/Chl *a* ratio ($P = 0.92$).

3.1.2. A. carterae

UV-exposed cultures had significantly lower Chl *a* concentrations than did PAR-only cultures ($P = 0.002$), with concentrations being on average 8% lower in UV-exposed samples throughout the experimental period (Fig. 2a). DMS concentration varied between 384 and 631 nmol L^{-1} for PAR-only samples and 321 and 631 nmol L^{-1} for PAR + UV samples (Fig. 2b). DMS/Chl *a* remained relatively stable after an initial decrease over the first 12 h ($P = 0.017$; Fig. 2c), and the PAR + UV treatment had no effect on DMS/Chl *a* ($P = 0.68$). The PAR + UV treatment had lower DMSPp/Chl *a* than that of the PAR-only samples ($P = 0.049$), and the UV-exposed samples had consistently lower DMSPp/Chl *a* ratios after 60 h of the experiment, with values being 25% lower than those in the PAR-only treatment by the end of the experiment (Fig. 2d). DMSOp/Chl *a* varied between 0.8 and 1.6 nmol DMSO μg^{-1} Chl *a*, but there were no differences in the DMSOp/Chl *a* ratios between the UV and non-UV treatments ($P = 0.34$).

3.1.3. T. oceanica

The maximum quantum yield of PS II (Fv/Fm) became lower with time, and UVR-exposed samples had significantly lower Fv/Fm than non-UV-exposed samples ($P = 0.017$; Fig. 3a). Nitrate addition, on the other hand, had no significant effects on Fv/Fm ($P = 0.11$). Intracellular Chl *a* concentrations (i.e. Chl *a*/cell volume) were significantly different between UV and non-UV-exposed treatments ($P = 0.001$), as well as between low and high nitrate treatments ($P = 0.001$), with UV exposure and reduced nitrate decreasing the concentrations (Fig. 3b). Both UV and nitrate treatments had significant main effects on intracellular DMSPp concentration (i.e. DMSPp/cell volume) with UV exposure and enhanced nitrate decreasing the concentration ($P = 0.004$ and 0.002, respectively; Fig. 3c). These effects, however, were complex and related to each other and to the sampling time in the experiment. Namely, exposure to UV tended to reduce intracellular DMSP concentration only on the two last sampling times of the experiment and under low nitrate availability (Fig. 3). The range of DMSOp/Chl *a* was 0.20–1.3 and 0.19–0.88 nmol DMSO μg^{-1} Chl *a* in PAR + UV and PAR-exposed cultures, respectively.

The growth rates of PAR/HN, PAR/LN, UV/HN and UV/LN, in terms of cell volume, during the exponential growth were $\mu' = 0.36$, 0.27, 0.18, and 0.16 d^{-1}, respectively. Cell volume was significantly different between UV and non-UV-exposed samples, as well as between high and low nitrate samples, with UV exposure decreasing and higher nitrate availability increasing cell volume ($P = 0.002$ and 0.005, respectively; Fig. 3d). Based on the cell number and cell volume, PAR-only samples reached the growth peak around 24–36 h after the inoculation (Fig. 3d and e). UV-treated samples continued to grow throughout the experimental period; however, the growth was lower than that of PAR-only treatments.

4. Discussion

Negative effects of UVR and low nitrogen were observed as physiological responses of phytoplankton: UVR reduced Chl *a* in cultures of *A. carterae* and *T. oceanica*, reduced Fv/Fm, and the growth rate of *T. oceanica*, while low nitrate treatment resulted in lower Chl *a* and growth rate but did not affect Fv/Fm of *T. oceanica*. These negative effects of UVR and low nitrate were in accordance with many previous reports (Garde and Cailiau, 2000; Bucciarelli and Sunda, 2003).

Both DMS concentration and Chl *a*-normalized DMS were higher in the UVR-exposed Gulf of Mexico water for the first 38 h despite the probable higher DMS photolysis promoted by UVR

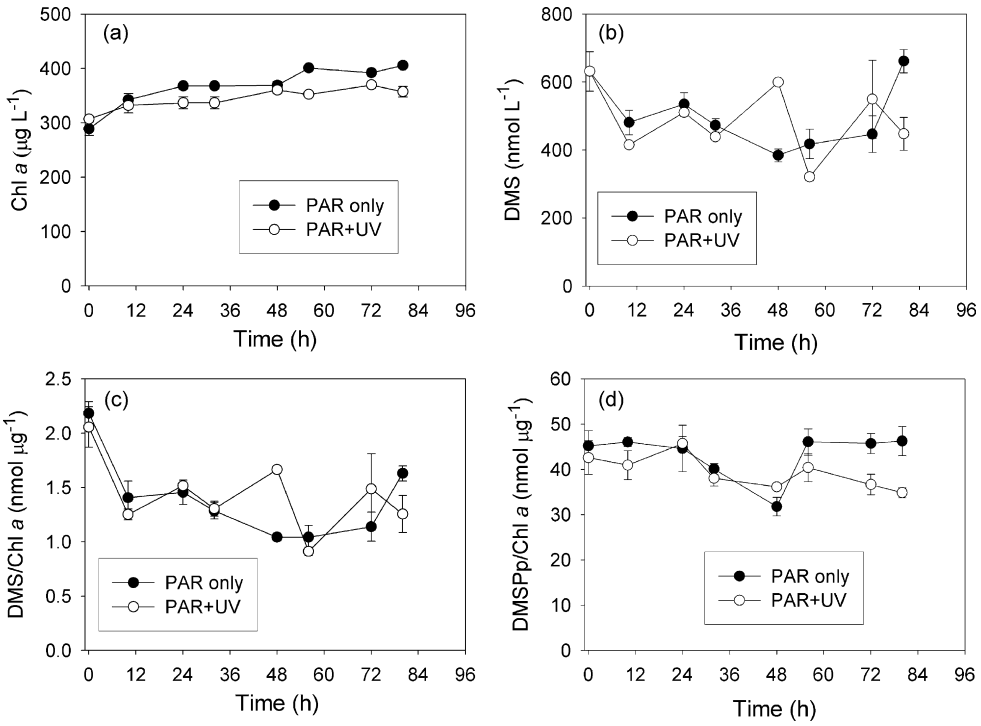

Fig. 2. Effects of UVR on Chl *a* (a), and DMS concentrations (b), Chl *a*-normalized DMS (c) and DMSPp (d) in *A. carterae* cultures. The cultures were incubated under cool white fluorescent lights (PAR-only) or fluorescent lights plus UVA bulbs (Q-Panel Co.).

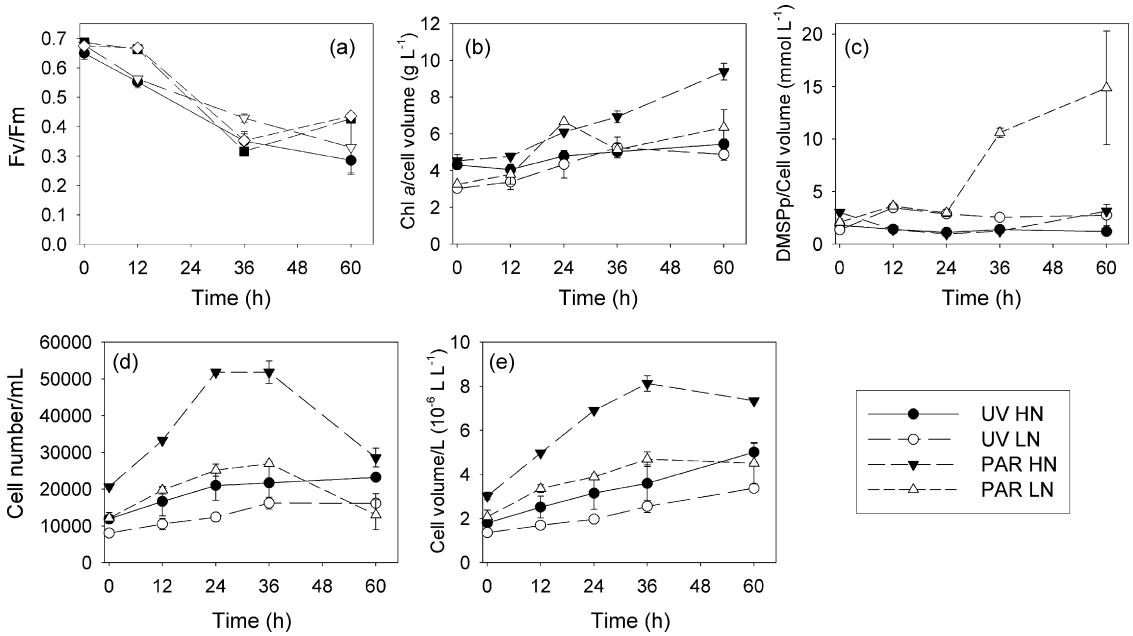

Fig. 3. Effects of UVR and nitrate concentration on Fv/Fm, cell volume normalized Chl *a* and DMSPp and cell number and volume in cultures of *T. oceanica*. The cultures were grown in high nitrate media (HN; 30 mM) or low nitrate media (LN; 5 mM), and incubated under cool white fluorescent lights (PAR-only) or fluorescence lights plus UVA bulbs (Q-Panel Co.).

(Toole et al., 2003). However, DMS/Chl *a* was nearly identical on days 3 and 4, and *A. carterae* showed very similar DMS/Chl *a* ratios between the UV and non-UV treatments throughout the experiment. Higher DMS/Chl *a* in the UV-exposed samples of the Gulf of Mexico water may have been caused by damage to cell membranes which would have resulted in the reaction of DMSP with DMSP lyase enzymes to produce DMS. Elevated levels of DMS due to grazing, viral lysis, and shear stress have been reported (Wolfe and Steinke, 1996; Malin et al., 1998; Wolfe et al., 2002), and membrane damage was one of the common effects by these stresses. Higher DMS concentrations could also result from stimulated DMSP cleavage to counteract UV-induced oxidative stress, but if this occurred, it did not consume a significant fraction of the cellular DMSP as Chl *a*-normalized DMSP did not decrease concomitantly with the increase in Chl *a*-normalized DMS in the Gulf of Mexico water experiment.

UV-exposed cultures of *A. carterae* and *T. oceanica* had lower DMSPp/Chl *a* or intracellular DMSPp concentrations than PAR-only samples, and that impact tended to occur late in the experiment (after 60 h for *A. carterae* and 36 h for *T. oceanica*). Our finding of lower DMSP in UV-exposed samples is in contrast to results found in several published studies. For example, working with *E. huxleyi* (CCMP374), Sunda et al. (2002) observed higher DMSP/cell volume ratios when cultures were exposed for 3 d to UVR + PAR as compared with PAR-only. In another study, UVR had no effects on the intracellular DMSP concentration of *E. huxleyi* (strain L) after 2 d of UV exposure despite evidence for some DNA damage (van Rijssel and Buma, 2002). Thus, the effects of UVR may be species specific or time dependent, and perhaps dependent on longer-term acclimation responses.

DMSPp/Chl *a* and DMSPp/cell volume were generally higher or similar to the non-UV treatments for the first 12–24 h in our study; thus, UVR may have stimulated the production of DMSP in the short term. However, the cumulative effect of UVR may have eventually reduced the DMSP production or increased DMSP loss, potentially due to membrane damage, elevated enzymatic cleavage or reactions with ROS, which would have exceeded the production rate in the longer time scale. This could explain why the reduced DMSP concentrations in UV-exposed treatments in our experiments occurred late in the experiments. Other than direct effects of UV, another mechanism that could explain the decrease in DMSP concentrations with UV exposure could be the production of ROS. DMSP and its cleaved products, DMS and acrylate, neutralize parts of the UV-induced ROS and reduce oxidative stress in the cell (Sunda et al., 2002). Indeed, DMSP and its breakdown products could constitute an efficient antioxidant system, which can scavenge hydroxyl radicals as efficiently as some known antioxidants, such as glutathione and ascorbate (Sunda et al., 2002).

Nevertheless, the experiment with *T. oceanica* cultures indicates that exposure to UV radiation suppressed intracellular DMSP concentration especially when nitrate availability was low. The N:P ratio of the high and low nitrate media were 24 and 4.9, respectively, and the growth of phytoplankton in low N media was limited by nitrogen availability because of their lower N:P ratio than the Redfield ratio (N:P = 16:1). Intracellular DMSP concentrations reached much higher values in the PAR-only, low nitrate cultures than in other cultures during the second half of the experiment. Those high values were likely due to severe nitrogen limitation in the cultures. Indeed, the phytoplankton in those cultures reached the growth peaks right before DMSP started to accumulate, suggesting that nitrogen depletion resulted in higher DMSP concentrations. An on-deck nutrient addition experiment using oligotrophic Sargasso Sea water provided evidence for a relationship between nutrient availability and DMSP (Harada et al., 2004). Additions of ammonia and phosphate resulted in 13-fold Chl *a* increase, whereas Chl *a*-normalized DMS, DMSP and DMSP lyase activity decreased by 15-, 6- and 7-fold, respectively. The results of the on-deck experiment suggest that nutrients were, in fact, limiting and increased nutrients availability reduced DMS and DMSP concentrations. Nitrate limitation is known to induce DMSP accumulation, more so than CO_2, P and Si limitations (Bucciarelli and Sunda, 2003). Thus, ammonia addition, not phosphate, likely contributed the reduction of the DMS and DMSP concentrations in

the on-deck incubation experiment. PAR-only, high nitrate cultures of *T. oceanica* in the present study had higher N:P ratio than the Redfield ratio and featured low DMSP concentrations and no significant response to UV exposure, possibly because no major nitrogen limitation occurred in these treatments. These results suggest that UV exposure could significantly reduce the concentration of DMSP in phytoplankton cells through, for instance, damage to cells or reaction with hydroxyl radicals to reduce oxidative stress, but only if pre-exposure concentrations of DMSP are high due to other sources of stress, such as nitrogen limitation.

The DMSP antioxidant system may be very important in nitrogen-limited environments. Phytoplankton produce a variety of antioxidant enzymes, such as superoxide dismutase, catalase, ascorbate peroxidate and glutathione reductase (Roy, 2000; Rijstenbil, 2002). These antioxidant enzymes require nitrogen. For phytoplankton under nitrogen-limited condition, synthesis of DMSP from methionine could produce N-free antioxidants and recycle nitrogen (Sunda et al., 2007). High solar radiation and low nutrient environments are typical characteristics of offshore waters, such as the Sargasso Sea, during the summer. Because Chl *a*-normalized DMS and DMSP concentrations were high near the surface of the ocean and from late spring to early fall coinciding with water column stratification (Belviso et al., 1993; Simó et al., 1995; Dacey et al., 1998), light intensity and nutrient limitation may be important factors controlling DMSP and other dimethylated sulfur compounds in many areas of the ocean. These observations, along with the results of this study, suggest that species in high light, low nutrient environment may have high DMSP concentrations, however, increases in UVR in such low nitrate environments could result in low DMSP concentration in some species possibly due to damage to cell, elevated DMSP cleavage or reactions with ROS, which in turn could result into large production of DMS and further oxidation to DMSO. In contrast, in eutrophic oceanic areas where Chl *a*-normalized DMSP concentrations would not be as high, increases in UV would not have such a large impact on DMSP concentration.

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