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Research Article

Effects of solar radiation on the fate of dissolved DMSP and conversion to DMS in seawater

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Abstract. The effect of ultraviolet radiation (UVR) and photosynthetically-active radiation (PAR) on the conversion of dissolved dimethylsulfoniopropionate (DMSPd) to dimethylsulfide (DMS) was studied in coastal, shelf and open ocean waters. Unfiltered and 0.8 μm filtered seawater samples were incubated in the dark or exposed to solar radiation for ~6 h followed by post-exposure, dark incubations with tracer additions of ^{35}S-DMSPd. End-products resulting from ^{35}S-DMSPd metabolism were quantified, including ^{35}S-DMS, total volatile ^{35}S and particle-assimilated ^{35}S. Exposure of productive coastal and shelf waters of the Gulf of Mexico to UVR+PAR inhibited the initial rates of ^{35}S-DMSPd consumption and the rates of ^{35}S assimilation into cellular macromolecules by 12 to 87 % and 13 to 81 % respectively, compared to dark controls. After 24 h of post-exposure, dark incubation, however, the assimilation of ^{35}S in the UVR+PAR treatments was the same as observed in dark controls. In contrast, the ^{35}S-DMS yield from DMSPd consumption was always higher in UVR+PAR treatments than in dark controls after 24 h post-exposure, dark incubation. Exposure of mesotrophic Mediterranean Sea or oligotrophic Sargasso Sea water samples to UVR+PAR resulted in variable effects on DMS yields, with two out of four experiments showing lower, and two out of four showing higher DMS yields from ^{35}S-DMSP compared with dark controls. In the Gulf of Mexico and Sargasso Sea, the higher ^{35}S-DMS yields caused by UVR+PAR exposure were offset by strong inhibitory effects of UVR+PAR on ^{35}S-DMSPd consumption rates, leading to lower ^{35}S-DMS production overall. When DMS production from DMSPd was compared to DMS production from total DMSP, we found that only 20 to 75 % of the produced DMS came from DMSPd, in one case with the lowest contributions from DMSPd in UVR+PAR treatments. Our results suggest that UVR exposure is likely an important factor promoting higher DMS yields from DMSPd in productive coastal waters, and that a substantial fraction of DMS production comes from non-DMSPd-derived sources.

Key words. Sulfur cycle; microbial community; bacteria; UVR; DMSP; DMS.

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Introduction

Dimethylsulfide (DMS) is a volatile organic sulfur compound that is involved in the transfer of sulfur from the oceans to the atmosphere (Lovelock et al., 1972). Interest in the biogeochemical cycling of DMS and its precursor, dimethylsulfoniopropionate (DMSP), has been stimulated by the hypothesis that biological DMS production, and its ultimate emission to the atmosphere, could affect the Earth's radiation budget and influence global climate via a negative feedback mechanism (Shaw, 1983; Charlson et al., 1987). Phytoplankton were initially thought to be the major source of DMS, but it is now recognized that a complex web of ecological, physical and biogeochemical processes control the production of DMS and ultimately its emission to the atmosphere (Simó, 2001).

Oceanic DMS originates almost exclusively from the degradation of DMSP, an osmolyte produced by various phytoplankton species (Keller et al., 1989). Conversion of DMSP to DMS is catalyzed by lyase enzymes, which are found in some phytoplankton species (Stefels and Boekel, 1993; Steinke and Kirst, 1996; Wolfe and Steinke, 1996; Steinke et al., 1998) and also diverse bacteria (Taylor, 1993; Todd et al., 2007). Some DMSP-producing phytoplankton have been observed to degrade DMSP by means of intracellular or exomembrane lyases, yielding DMS and acrylate, whereas some non-DMSP producing or low-DMSP producing phytoplankters appear to take up and assimilate DMSP-sulfur through an unidentified biochemical pathway (Vila-Costa et al., 2006). Heterotrophic bacteria can degrade dissolved DMSP (DMSPd) via at least two different pathways: lyase cleavage and demethylation/demethiolation, with the latter process diverting DMSP-sulfur away from DMS production (Taylor and Gilchrist, 1991; Kiene et al., 2000; Howard et al., 2006). Dissolved DMSP is formed during grazing and viral lysis of phytoplankton (Dacey and Wakeham, 1986; Malin et al., 1998) and most DMSPd appears to be demethylated by bacteria rather than converted to DMS (see review by Kiene et al., 2000). The yield of DMS from DMSP consumption (moles of DMS produced per mole of DMSP consumed) varies significantly from 2 to 100%, and is therefore one important determinant affecting DMS production, and ultimately how much is emitted to the atmosphere (Simó and Pedrós-Alió, 1999; Kiene et al., 2000). Simó and Pedrós-Alió (1999) found an empirical relationship between the DMS yield and the mixed layer depth, with higher yields in shallower mixed layers. They postulated that meteorological conditions (e.g. UVR, wind speed) govern the DMS yield, both from the DMSPd pool and the total DMSP pool. However, at present it is not known whether shifts in the DMS yield occur under high solar radiation doses.

Microbial turnover of DMSPd can be very fast (turnover times of hours) in highly productive systems (Kiene, 1996b; Ledyard and Dacey, 1996; Van Duyl et al., 1998; Kiene and Linn, 2000a), and bacteria can use DMSPd as a major source of reduced sulfur for protein amino acid synthesis (Kiene et al., 1999). The assimilation of sulfur from DMSPd is linked to the demethylation pathway and the production of methanethiol. Therefore, bacterial growth and sulfur demand may influence how much DMSP is demethylated versus cleaved to DMS (Kiene et al., 2000). High doses of solar radiation can inhibit the growth and activity of marine bacteria (Herndl et al., 1993; Aas et al., 1996) and also the consumption of DMSP and DMS (Slezak et al., 2001; Toole et al., 2006). Thus, high doses of UVR and PAR might be expected to affect the sulfur demand, and perhaps the partitioning of DMSP degradation.

In the present study, we examined the effects of solar radiation (UVR+PAR and PAR alone) on the fate of DMSPd and yield of DMS from this pool in coastal, shelf and open ocean waters. We also compared the production of DMS from dissolved DMSP (using ^{35}S-DMSPd tracer) with total DMS production in Gulf of Mexico water.

Material and methods

Study sites and sampling methods

Sea water samples were collected from the coastal Gulf of Mexico near Dauphin Island, Alabama (30° 14.78 N, 87° 50.16 W) and from a shelf site in the Gulf of Mexico (30° 00.62 N, 88° 07.58 W). Additional samples were collected from a coastal site in the Mediterranean Sea near Blanes, Spain, and from two open ocean sites in the Sargasso Sea near Bermuda. Information on the sampling locations and background concentrations of total, particulate and dissolved DMSP and DMS are given in Table 1. Water was collected either by hand with a 5% HCl-rinsed bucket (coastal sites) or with Niskin bottles attached to a CTD rosette (oceanic sites). Water samples were passed gently through a 200 μm Nitex screen by gravity to remove large zooplankton and stored in polycarbonate containers at the *in situ* temperature in the dark until processed (< 3 h).

General experimental design

To test the effect of solar radiation exposure on DMSP fate, we exposed unfiltered or 0.8 μm-filtered seawater to various light treatments for 4 to ~6 h, and

Table 1. Sampling dates, locations, incubation time and initial water characteristics for all experiments carried out to investigate the effect of solar radiation on ^{35}S-DMSPd consumption and ^{35}S-DMSPd partitioning. DI, Dauphin Island; DMSPt = total DMSP; DMSPd = dissolved DMSP; and DMSPp = particulate DMSP (calculated as the difference between total and dissolved DMSP; Kiene and Slezak, 2006). All samples were gently screened by gravity through a 200 μm Nitex net, except for the 0.8 μm filtered samples. N.D. = not determined.

Date	Sample location	Water temperature °C	Sampling time Local time	Incubation time Local time	Sample depth m	Chlorophyll a μg l^{-1}	DMSPt nM	DMSPd nM	DMSPp nM	DMS nM
Gulf of Mexico										
7/23/2002*	DI pier	32	10:31	11:15–17:00	0	N.D.	34.3	1.3	33.0	N.D.
8/7/2002*	DI pier	30	10:05	11:20–15:30	0	N.D.	38.4	1.5	36.8	N.D.
8/9/2002*	DI pier	29	11:05	11:40–16:30	0	N.D.	39.7	2.3	37.4	N.D.
8/21/2002$^+$	DI pier	31	10:29	11:10–15:40	0	N.D.	25.2	1.3	24.0	N.D.
8/30/2002	DI pier	31	3:31	11:15–16:30	0 (0.8 μm filtrate)	N.D.	N.D.	N.D.	N.D.	N.D.
9/5/2002$^+$	DI pier	31	9:15	11:00–16:15	0	6.52	42.5	2.7	39.9	N.D.
9/12/2002$^+$	N 30° 00.62 W 87° 50.16	30	8:30	11:15–16:45	0	0.35	28.2	2.3	25.8	1.8
9/12/2002$^+$	N 30° 00.62 W 87° 50.16	30	8:30	11:25–16:55	0 (0.8 μm filtrate)	0.35	N.D.	N.D.	N.D.	N.D.
10/16/2002$^+$	DI pier	27	7:30	10:00–16:30	0	N.D.	11.5	0.7	10.8	0.6
Mediterranean Sea										
8/5/2003	N 41° 39.90 E 2° 48.03	25	8:00	10:00–14:00	0.5	0.34	24.0	1.6	22.4	5.9
8/7/2003	N 41° 39.90 E 2° 48.03	24	8:00	10:00–14:00	5	N.D.	N.D.	6.2	N.D.	5.1
Sargasso Sea										
4/15/2002	N 31° 30.02 W 69° 00.01	21	6:30	10:40–17:10	0.5	0.05	12.3	1.8	10.5	2.1
7/17/2004	N 30° 46.40 W 65° 48.40	27	4:15	9:10–17:25	10	0.04	10.5	1. 6	9.0	2.2

* Two treatments (UVR+PAR and dark) in triplicates
$^+$ Three treatments (UVR+PAR, PAR and dark) in duplicates

subsequently incubated those samples in the dark for 2 to 24 h, during which time ^{35}S-DMSP transformations were measured. We chose this post–exposure, dark incubation design because the effects of solar radiation on microbial communities typically depend on the cumulative dose of absorbed radiation (Neale et al., 1998; Jeffery et al., 2000), and we deemed it better to determine the fate of DMSP after light treatments had had enough time to produce discernable effects. An alternative approach would have been to measure DMSP transformations during exposure to sunlight, but such an approach has several disadvantages for DMSP fate measurements. First, DMS photolysis would have made it difficult to quantify the gross production of DMS. Second, if ^{35}S-DMSPd was added to samples exposed to sunlight, it is possible that the DMSP-tracer would have been consumed to a significant degree before the cumulative effect of solar radiation on DMSP loss were evident. The main disadvantage of our post-exposure, dark incubations was that recovery of microbial process undoubtedly occurred to a certain extent during dark incubations (Kaiser and Herndl, 1997).

Gulf of Mexico UVR and PAR experiments

Dissolved ^{35}S-DMSP degradation time course and fate. We used 0.8 μm filtered seawater (containing mainly bacteria) from the Gulf of Mexico (September 12, 2002; Table 1) to study the degradation and fate of ^{35}S-DMSPd after treatment with solar radiation. The 0.8 μm filtered water sample was obtained by sequential gravity filtration through an A/E glass fiber filter (Pall-Gelman, 1 μm, 142 mm diameter) and a 0.8 μm polycarbonate filter (Millipore ATTP, 142 mm) using an in-line filter holder. The filtered seawater was distributed into 40 ml quartz tubes and subsequently allocated into three treatments. One treatment (UVR+PAR, 10 quartz tubes) remained uncovered and was exposed to full spectrum solar radiation. A second treatment (PAR, 10 quartz tubes) was covered with clear acrylic glass (Plexiglas type UF3, Rohm-Haas, PA, USA), which selectively removed UVR leaving PAR only (Booth et al., 2001). A third treatment was wrapped in several layers of aluminum foil and served as the dark control (10 replicate quartz tubes). All samples were exposed to sunlight for 5–6 h around solar noon in a shallow flow-through, water bath to maintain samples at their *in situ* temperature. After exposure to sunlight, the seawater in five quartz tubes from the same treatment was combined into a

125 ml Teflon bottle. This was repeated for all treatments yielding duplicate Teflon bottles per treatment, with sufficient water volume (100 ml) in each Teflon bottle for subsequent time course sampling. Teflon bottle samples were amended with dimethyldisulfide (DMDS, Sigma Aldrich) to a final concentration of 200 nM to inhibit DMS consumption (Wolfe and Kiene, 1993), treated with tracer levels (< 5 pM) of ^{35}S-DMSPd and incubated in the dark in a circulating water bath to maintain the *in situ* temperature. Post-exposure, dark incubations continued for up to 24 h during which time the consumption and fate of ^{35}S-DMSPd were determined at selected time points. For each time point, we quantified the residual ^{35}S-DMSPd, the assimilation of ^{35}S into trichloroacetic acid (TCA)-insoluble particulates (mainly proteins) and the production of total, volatile ^{35}S and ^{35}S-DMS (for details see *Analytical Methods*).

Consumption of ^{35}S-DMSPd and end product partitioning. In addition to time course experiments, nine experiments were performed with light-exposed Gulf of Mexico samples and dark controls in which consumption rate constants for ^{35}S-DMSPd were determined in 2 h post-exposure, dark incubations, while the assimilation of ^{35}S and the ^{35}S-DMS yield from ^{35}S-DMSPd degradation were measured with single, end-time point determinations after 24 h of post-exposure, dark incubation. The experimental design was similar to that described above for the time course experiment, with exposure of either two treatments (UVR+PAR and dark, each in triplicates) or three treatments (UVR+PAR, PAR and dark, each in duplicates) to solar radiation in a flowing water bath for 5–6 h, followed by post-exposure, dark incubations with ^{35}S-DMSPd. Total DMSP (DMSPt), DMSPd and DMS concentrations were determined at the end of the light exposure phase. Actinic UVB, UVA and PAR light doses for these Gulf of Mexico experiments are presented in Table 2. In two of the nine experiments (Aug 30 and Sep 12, 2002; Table 1), 0.8 μm-filtered water was used instead of unfiltered water to focus on the non-particle associated, free-living bacterial fraction of the microbial community. For details regarding ^{35}S-tracer methods and DMSP and DMS concentration determinations see *Analytical methods*.

Effects of light intensity on ^{35}S-DMSPd consumption and ^{35}S-DMS yield. On August 30, 2002, 0.8 μm filtered water from the coastal Gulf of Mexico (Dauphin Island pier) was used to test the effect of light attenuation on the degradation of DMSPd. Filtered water samples were distributed into 40 ml quartz tubes and exposed to surface solar radiation for ~5 h around solar noon in a flow through water bath. Neutral density screens (common window screen, transmission tested with radiometers) and aluminum foil were used to generate the following treatments, based on the % total surface solar irradiance: 0 % (3 layers of aluminum foil), 18 % (3 layers of screen), 35 % (2 layers of screen), 57 % (1 layer of screen) and 100 % (no screen). Degradation of ^{35}S-DMSPd, ^{35}S-DMS yields and ^{3}H-leucine incorporation (a general measure of bacterial activity) were determined in post-exposure, dark incubations (see *Analytical methods*).

Table 2. Light doses for experiments in the Gulf of Mexico, Sargasso Sea and the Mediterranean Sea. Doses are integrated over the incubation period and over the wavelength range for PAR, UVA and UVB. N.D. = not determined.

Date	Irradiation depth (m)	Light range PAR (mol m^{-2})	UVA (kJ m^{-2})	UVB (kJ m^{-2})
Gulf of Mexico				
7/23/2002	0	N.D.	N.D.	N.D.
8/7/2002	0	40.0	709	79.8
8/9/2002	0	45.4	839	90.4
8/21/2002	0	42.7	773	87.0
8/30/2002	0	48.4	795	87.5
9/5/2002	0	46.4	N.D.	N.D.
9/12/2002	0	49.0	768	80.2
10/16/2002	0	56.3	N.D.	N.D.
Mediterranean Sea				
8/5/2003	0	101.7	1519	82.3
8/7/2003	0	95.1	1439	78.0
Sargasso Sea				
4/15/2002	0	33.6	1061	49.6
	3	29.6	904	36.1
	9	22.8	661	19.2
	17	16.2	442	8.3
	29	9.7	250	2.4
7/17/2004	0	26.5[1]	1283	62.8
	5	21.9[1]	1005	36.2
	10	18.1[1]	794	20.9
	20	12.4[1]	508	7.0
	40	5.8[1]	225	0.8

[1] PAR range: 400–600 nm. Underestimation of about 25 % as compared to full PAR range (400–700 nm).

Mediterranean and Sargasso Sea UVR and PAR experiments

In addition to the experiments conducted with productive Gulf of Mexico water, experiments were also conducted to determine if the effects of UVR and PAR on DMSP degradation and DMS yield were similar in less productive waters.

^{35}S-DMSPd degradation in Mediterranean seawater. Water from a shallow, mesotrophic station of the northwestern Mediterranean Sea located ~800 m off-

shore of Blanes, Spain (Blanes Bay Microbial Observatory, 41° 39.90'N, 2° 48.03'E; maximum depth, ~20 m) was used to determine the effect of different solar spectral treatments on DMSPd degradation in samples from the surface mixed layer (0.5 m; Aug 5, 2003) and below it (5 m; Aug 7, 2003). Water for the experiments was collected immediately after sunrise and screened through a 200 μm mesh to eliminate large zooplankton. This water was distributed into 100 ml spherical quartz glass bottles and exposed to: 1) full spectrum solar radiation (UVR+PAR), 2) UVA+PAR using Mylar D film (DuPont, VA, USA) to block UVB, 3) PAR using a vinyl chloride foil (CI Kasei Co., Tokyo, Japan) and 4) dark controls that were wrapped in three layers of aluminum foil. For more information on the optical screens used see Alonso-Saez et al. (2006) and Sommaruga et al. (2005). Samples were exposed to sunlight for 4 h around solar noon in a water bath, and the degradation and fate of ^{35}S-DMSPd were measured in post-exposure, dark incubations (see *Analytical methods* for details). The actinic solar radiation in the UVB, UVA and PAR was very similar for both experiments (Table 2).

Depth dependent ^{35}S-DMS yields from ^{35}S-DMSPd in the Sargasso Sea. Two experiments were conducted to determine the ^{35}S-DMS yield in seawater samples that were suspended at different depths in the water column and exposed to ambient solar radiation for 7–8 h. Seawater used for this study was collected in the oligotrophic Sargasso Sea at two locations and on two different dates. On each date, water was collected between 0400 and 0630, local time from a single depth in the surface mixed layer (0.5 m on April 15, 2002 and 10 m on July 17, 2004). Unfiltered seawater was distributed into quartz tubes that were incubated at five depths in the mixed layer, employing a free-floating drifter array as described in Toole et al. (2006). During the 4 to 5 h from sample collection to exposure on the free-floating drifter array, samples in quartz tubes were always kept in the dark at *in situ* temperature. Samples were exposed to sunlight from 1040–1710 local time, on April 15, 2002 and from 0910–1725 local time on July 17, 2004. Incubation depths and solar radiation flux at each depth are given in Table 2. Dark controls were wrapped with 3 layers of aluminum foil and incubated in a deckboard, flow through seawater incubator. After the *in situ* exposure, samples were treated with ^{35}S-DMSPd and the yield of ^{35}S-DMS was determined in post-exposure, dark incubations (for details regarding ^{35}S-DMS yield determinations see *Analytical methods*).

DMS production from total versus dissolved DMSP in the Gulf of Mexico

Two experiments were conducted to compare the DMS production from DMSPt and DMSPd degradation and effect of solar radiation on the ratio between both. Water for these experiments was collected from the coastal Gulf of Mexico (Dauphin Island pier, October 16, 2002) and from a shelf site in the Gulf of Mexico (September 12, 2002). Unfiltered water samples were distributed into 1 L FEP Teflon bottles in three treatments: UVR+PAR (uncovered), PAR (UF3 Plexiglas-covered) and aluminum foil-wrapped dark controls. Duplicate bottles for each treatment were exposed to surface sunlight for 5–6 h in a flowing water bath to maintain the ambient seawater temperature. The 1 L Teflon bottles were used instead of quartz tubes because larger sample volumes were needed to determine the DMS production from DMSPt (Simó et al., 2000). FEP Teflon is slightly less transparent to UVR than quartz glass, so we underestimated the effects of UVB and to a lesser extent of UVA by using Teflon bottles (P. Neale, pers. comm.). After exposure to sunlight, all treatments were treated with DMDS (200 nM final concentration) to inhibit DMS consumption and incubated in the dark in a water bath for 24 h. During the post-exposure, dark incubation, we determined the time course changes in DMS concentrations. Additionally, sub-samples from light-exposed samples and dark controls were taken immediately after the exposure phase and used to determine the ^{35}S-DMSPd consumption rate and ^{35}S-DMS yield in post-exposure, dark incubations (see *Analytical methods* for details).

Analytical methods

^{35}S-DMSPd tracer measurements. DMSPd consumption rate constants, DMS yield from DMSPd and sulfur assimilation from DMSPd were measured with tracer additions of ^{35}S-DMSPd (Kiene and Linn, 2000b) in post-exposure, dark incubations. DMSPd consumption rate constants (^{35}S-k_{DMSP}) were determined by following the loss of ^{35}S-DMSPd over time. Briefly, water samples were transferred into 30 ml Teflon bottles and tracer amounts (< 5 pM) of ^{35}S-DMSPd were added to give about 1000 dpm·ml^{-1} sample. The Teflon bottles were closed, gently mixed and then incubated at *in situ* temperature in the dark. At discrete time points, a 4 ml sub-sample was taken from each Teflon bottle and transferred into a polyethylene vial containing 40 μl of 20 % sulfuric acid (final pH < 2). The H_2SO_4 preserved the DMSP, stopped bacterial activity and oxidized ^{35}S volatiles to non volatiles (Curran et al., 1999; Kiene and Slezak, 2006). Preserved samples were stored for > 24 h before analysis. For analysis of the remaining

^{35}S-DMSPd, a 3 ml sub-sample from each preserved time point sample was transferred into a 60 ml serum bottle. The bottle was sealed with a rubber stopper fitted with a plastic cup that held a glass fiber filter soaked with 0.2 ml of 3 % H_2O_2 that served as a trap for volatile ^{35}S-DMS. To each bottle, 0.2 ml 5 N NaOH was injected through the stopper to quantitatively cleave ^{35}S-DMSPd to ^{35}S-DMS and the bottles were placed on a rotary shaker and shaken at 100 rpm for $>$ 6 hr (Kiene and Linn, 2000b). After trapping, filters were placed into 6 ml scintillation vials with 5 ml of Ecolume scintillation fluid. The scintillation vials were held for $>$ 12 hr to allow counts to stabilize before they were counted with a Packard Tri-Carb model 2500 TR scintillation counter. The DMSPd loss rate constant was calculated as the slope of the natural log of the fraction of remaining ^{35}S-DMSPd versus time. DMSP consumption rates were calculated by multiplying the first order rate constant by the initial DMSPd concentration, which was determined just before the tracer addition (see below).

The yield of DMS from ^{35}S-DMSPd and the assimilation of ^{35}S from ^{35}S-DMSPd into TCA-insoluble macromolecules were determined after the light treatments by transferring a sub-sample of water samples into 10 ml serum vials. DMDS was added to a final concentration of 200 nM to allow the determination of the gross ^{35}S-DMS production. The ^{35}S-DMSPd was added at tracer concentrations ($<$ 5 pM; ca. 1000 dpm ml^{-1}) and the vials were incubated at *in situ* temperature in the dark (for ~ 24 h) until $>$ 90 % of the ^{35}S-DMSPd was consumed. At the end of the incubation, 5 ml of each water sample was transferred into a 60 ml serum bottle that contained 0.1 ml of 10 % sodium dodecyl sulfate (SDS, stops bacterial activities) amended with 200 μM unlabeled DMSP to stop further uptake of ^{35}S-DMSP, and 0.05 ml 5,5-dithiobis(2-nitrobenzoic acid) (DTNB or Ellman's Reagent, –1 mg DTNB per ml of 50 mM TRISMA-HCl, pH 8, Sigma) to complex thiols, including methanethiol (Ellman, 1958; Riddles et al., 1983). Ellman's reagent does not complex DMS. Therefore, ^{35}S-DMS is the only volatile ^{35}S-containing compound likely to be present in the serum bottles containing Ellman's reagent. After transferring water samples to serum bottles, the bottles were quickly sealed with a rubber stopper fitted with a plastic cup holding a glass fiber filter soaked with 0.2 ml of 3 % aqueous H_2O_2 and processed further as described above. After trapping for $>$ 6 h, filters were placed into 6 ml scintillation vials with 5 ml of Ecolume scintillation fluid to determine the amount of ^{35}S-DMS produced.

A 5 ml sub-sample of the remaining water sample was vacuum filtered through a 0.2 μm Nylon filter and the filter was treated with trichloroacetic acid (TCA) as described in Kiene and Linn (2000b). Radioactivity remaining on TCA-rinsed filters was quantified by liquid scintillation counting, and represented sulfur assimilated into macromolecules (e.g., protein).

Procedures for the total ^{35}S-volatile production were the same as those for the DMS yield determination, except that the Ellman's Reagent was not added to the serum bottle (see also Kiene and Linn, 2000b). After the volatile degradation products derived from ^{35}S-DMSPd during the incubations were trapped, the residual ^{35}S-DMSPd in the sample was quantified by replacing the trapping filter with a new one, and adding 0.2 ml of 5 N NaOH through the stopper. The NaOH cleaved any remaining ^{35}S-DMSPd to ^{35}S-DMS, which was trapped onto the new H_2O_2-soaked filter in the plastic cup and subsequently counted (see above).

All ^{35}S product pool measurements were expressed as a fraction of the initial added amount of ^{35}S, which was determined by pipetting a 1 ml sub-sample of the water directly into a scintillation vial containing 5 ml scintillation fluid (Ecolume) and counted according to the method outlined in Kiene and Linn (2000b). Abiotic controls consisted of 0.2 μm-filtered seawater treated with ^{35}S-DMSPd. The counts of the ^{35}S product fractions obtained in the controls (generally, $<$ 0.5 % of the added tracer for volatiles and $<$ 1 % for assimilation) were used to correct the activities in unfiltered or 0.8 μm-filtered samples. We used a conservative trapping efficiency of 90 % to correct the volatile production, which might underestimate the MeSH production (Kiene and Linn, 2000b).

Bacterial leucine incorporation. Bacterial biomass production was measured by the incorporation of [^{3}H]-leucine into trichloroacetic acid (TCA)-insoluble material (Kirchman, 1993) in post-exposure, dark treatments. Additions of 20 nM [^{3}H]-leucine were made to triplicate 1.5 ml samples and one TCA-killed control, followed by a 1 h dark incubation at the *in situ* temperature. Samples were then processed according to the microcentrifugation method (Smith and Azam, 1992).

DMSP and DMS sampling and analysis. Samples for total DMSP (DMSPt) analysis consisted of whole water acidified to pH $<$ 2 with 50 % H_2SO_4 (Curran et al., 1999; Kiene and Slezak, 2006). The acid-preserved DMSPt samples were stored in 15 ml polypropylene centrifuge tubes for a minimum of 24 h, and sometimes up to 1 month, before analysis (see below).

Dissolved DMSP was collected by gravity drip filtration of 10 ml samples through 47 mm GF/F filters (Whatman). Care was taken to not let the filter become exposed to air during sample filtration.

Filtrate (5–7 ml) was collected directly into 15 ml centrifuge tubes containing 5 µl/ml sample of 50 % sulfuric acid and left for at least 24 hr (Kiene and Slezak, 2006). During the time when our measurements were made, the recently recommended small volume drip filtration (SVDF) procedure for DMSPd determination (Kiene and Slezak, 2006) had not yet been developed. Therefore, the DMSPd concentrations might, in some cases, be subject to artifactual overestimation (see *Discussion*).

Samples for DMS analysis were collected into 10 ml serum vials without headspace, and kept at the *in situ* temperature in the dark. Within 1 h after collection, 2–4 ml sub-sample was taken up into a glass syringe and gently filtered through a GF/F filter into a sparging tube. DMS was sparged from the water with a stream of helium and trapped in a loop of Teflon tubing immersed in liquid nitrogen (Kiene, 1996a). Trapped DMS was analyzed on a Shimadzu GC-14A gas chromatograph (GC) as described in Kiene and Hines (1995). Acidified DMSP samples (1–3 ml) were pipetted into 10 ml serum vials, 1 ml of 5 N NaOH was added to cleave DMSP into DMS, and vials were quickly sealed and incubated for ~ 3 h. The resulting DMS was purged into a cryotrap and quantified by GC as described above. All DMS and DMSP samples were analyzed in duplicate, with analytical precision <5 % for all samples.

Light measurements. The UVR and PAR were measured with different multi-channel radiometers, depending on the experiment. For the experiments conducted in the Mediterranean Sea, a PUV-501 (Biospherical Instruments Inc. (BSI), San Diego, CA, USA) was used (for details see Alonso-Saez et al., 2006 and Sommaruga et al., 2005). A SeaWiFS multichannel radiometer (SMSR, Satlantic, Halifax, Nova Scotia, Canada) was used in the Sargasso Sea in 2002 (Toole et al., 2006), and a Biospherical PUV-2510 was used during the 2004 Sargasso Sea experiments. For the Gulf of Mexico, a broadband radiometer equipped with sensors that integrated over the entire UVA and UVB spectral ranges was used (PMA 2100, sensors: UVA detector: PMA2110; UVB detector: PMA2106, Solar Light, Glenside, PA, USA). For comparison with the integrated data from the PMA 2100, the data from the multi-channel radiometer were extrapolated spectrally using a location- and month-specific UVR climatology model (Lubin et al., 1998) scaled to the measured wavelengths. For the two *in situ* drifter incubations (Sargasso Sea, 2002 and 2004), vertical profiles of spectral downwelling irradiance were measured several times throughout the day with a SeaWiFS profiling multi-channel radiometer (SPMR, Satlantic) and a Biospherical PUV-2500 radiometer, respectively. The light dose at each incubation depth was determined using the time course of surface irradiance attenuated with depth using downwelling attenuation coefficients ($K_d(\lambda)$) determined throughout the day (see Toole et al., 2006).

Results

Gulf of Mexico UVR and PAR experiments

Dissolved ^{35}S-DMSP degradation time course and fate. Results from a UVR-PAR exposure experiment with 0.8 µm-filtered Gulf of Mexico surface seawater in which the time course of ^{35}S-DMSPd degradation and fate was measured in post-exposure, dark incubation are shown in Figure 1. The rate of ^{35}S-DMSPd consumption in samples exposed to full spectrum radiation (UVR+PAR) was inhibited by 90 % (based on the first order loss rate constant) relative to dark controls (Fig. 1A). The PAR treatment caused an inhibition of 45 % compared to the dark control. Although the consumption rate of the added ^{35}S-DMSPd was substantially reduced in the UVR+PAR samples, the tracer was almost entirely consumed within 14 h (compared to 5 h in the dark and PAR treatment) (Fig. 1A).

The rate of ^{35}S assimilation from ^{35}S-DMSPd into TCA-insoluble particulates was inhibited by 87 % in the UVR+PAR treatment and 43 % in the PAR treatment relative to the dark controls. Despite this inhibition, the fraction of added ^{35}S-tracer assimilated into particles (48 and 52 %, UVR+PAR and PAR, respectively) was comparable to that observed in the dark controls (59 %, Fig. 1B) after incubation for 24 h when all the ^{35}S-DMSPd was consumed during post-exposure, dark incubations.

The initial rate of total volatile ^{35}S production from ^{35}S-DMSPd was inhibited by 82 % in the UVR+PAR treatment compared to the dark control (Fig. 1C), but was only marginally affected by PAR (8 %; Fig. 1C). The initial rapid accumulation of total volatile ^{35}S, to about 12 % of the added ^{35}S-tracer in dark controls, was followed by a period of slower decline until the total volatile ^{35}S fraction leveled off at about 4 % of the added ^{35}S-tracer for both the PAR treatment and dark control. This pattern of rapid increase followed by a decline of volatile ^{35}S was probably due to the biological and chemical consumption of methanethiol (MeSH), a major constituent of the volatile ^{35}S pool (Kiene and Linn, 2000b). Despite the lower production of volatile ^{35}S, the total volatile ^{35}S fraction in the UVR+PAR treatment eventually surpassed that observed in the dark and PAR treatments and the levels did not decline appreciably after reaching a maximum at 5 h (Fig. 1C).

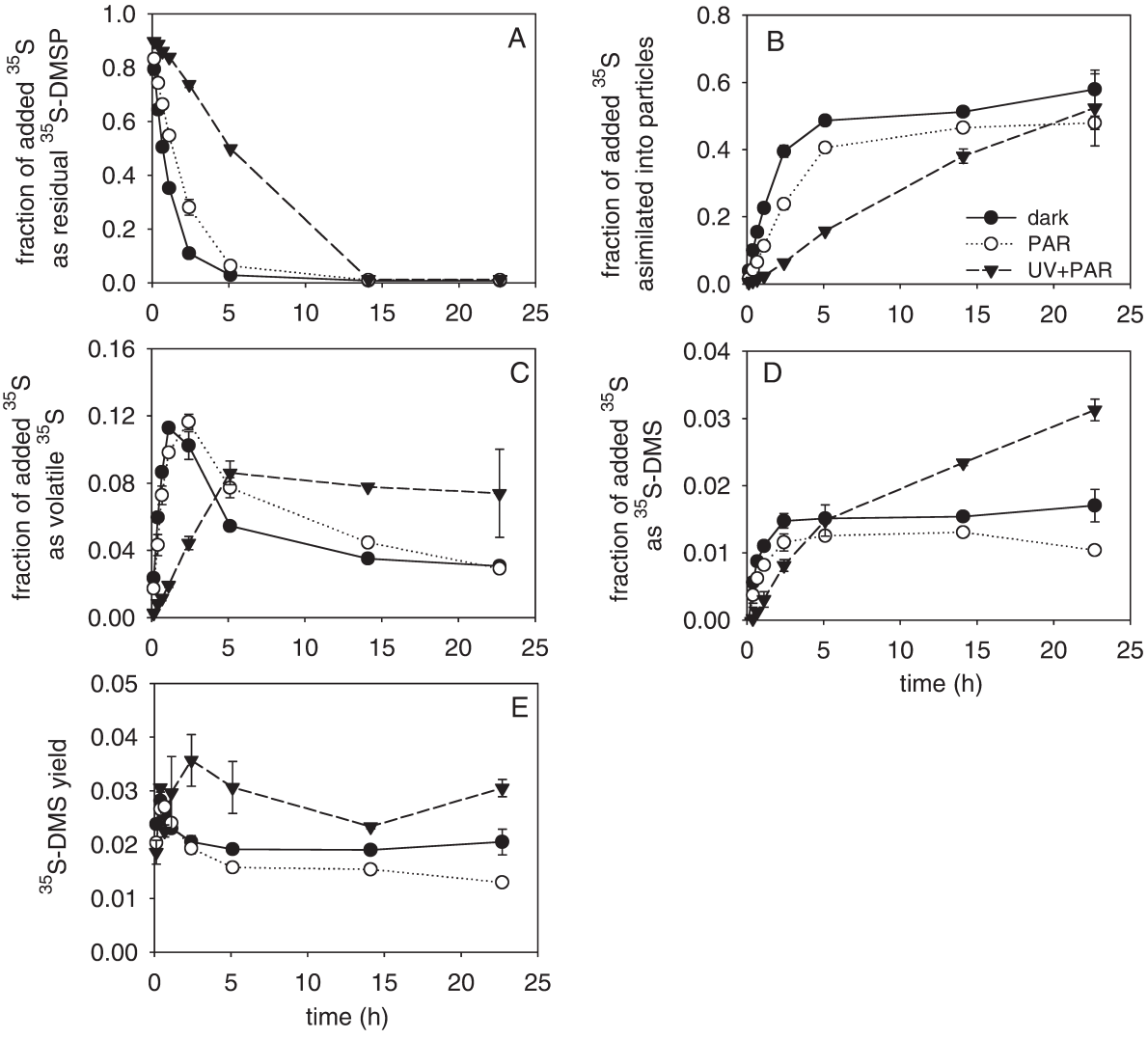

Figure 1. Time course of the degradation and fate of ^{35}S-DMSPd in 0.8 μm-filtered surface seawater from the Gulf of Mexico shelf (September 12; Table 1) after exposure of replicate samples to three different surface light regimes (UVR+PAR, PAR, and dark controls) for ~6 h. A) Fraction of added ^{35}S as residual ^{35}S-DMSP; B) Fraction of added ^{35}S assimilated into TCA-insoluble particles; C) Fraction of added ^{35}S converted to volatile ^{35}S; D) Fraction of added ^{35}S converted to ^{35}S-DMS; and E) Fraction of consumed ^{35}S-DMSPd converted to ^{35}S-DMS (i.e. ^{35}S-DMS yield). Values are means of experimental duplicates and error bars represent the range of the data.

The production rate of ^{35}S-DMS (on average a 20 % subfraction of total volatile ^{35}S pool) was initially inhibited by 66 % after exposure to UVR+PAR, compared to the dark control (Fig. 1D). The ^{35}S-DMS continued to accumulate in the UVR+PAR treatment until 23 h whereas the accumulation ceased after 3 h in the PAR treatment and dark control. The accumulation of ^{35}S-DMS in the UVR+PAR treatment eventually exceeded that in the PAR treatment and dark controls by factors of 3 and 1.8, respectively. When normalized to the amount of ^{35}S-DMSPd consumed, the DMS yield from DMSP consumption was higher in the UVR+PAR treatment (mean of 3 %) compared to the PAR and dark treatments (means of ca. 2 %; $p < 0.05$, Tukey's test; Fig. 1E).

The time course results presented above obtained with 0.8 μm-filtered seawater, were typical of four such experiments, including two that were conducted with unfiltered seawater from the Gulf of Mexico. As the patterns were not substantially different between unfiltered and 0.8 μm-filtered samples, the effect of UVR and PAR on ^{35}S-DMSPd degradation was likely due to changes in bacterial activity.

^{35}S-DMSPd degradation and end-product partitioning. Results of nine experiments testing the effect of solar radiation on ^{35}S-DMSPd consumption and ^{35}S-DMSPd end-product partitioning in either 0.8 μm filtered or unfiltered Gulf of Mexico seawater are summarized in Figure 2. Results are shown as the

ratio of each parameter value (e.g., DMS yield) in the PAR or UVR+PAR treatment to the value in the corresponding dark control, expressed as a percentage, and plotted against the value of the parameter obtained in the dark control. When expressed in this fashion, the first order loss rate constant for DMSPd consumption (^{35}S-k_{DMSPd}) was inhibited, on average (± range), by 90 ± 7 % in the UVR+PAR treatments compared to dark controls ($p < 0.05$, Tukey's test), but inhibition was only 19 ± 13 % in the PAR treatment, and these values were not significantly different from the dark control ($p > 0.05$, Tukey's test, Fig. 2A). Since DMSPd concentrations tended to increase during incubations, DMSP consumption rates (^{35}S-k_{DMSPd} x [DMSPd], Fig. 2B) were inhibited by UVR+PAR to a lesser extent, on average (± range), 74 ± 17 % ($p < 0.05$, Tukey's test) than rate constants (compare solid symbols in Figure 2A and 2B). In contrast, ^{35}S-DMSPd consumption rates in the PAR treatment were generally the same as, or in some cases higher than in the dark control (Fig. 2B). Unlike the strong inhibition of the initial ^{35}S-assimilation rate as shown in Figure 1B, the fraction of ^{35}S-DMSPd assimilated into macromolecules after 24 h of post-exposure, dark incubations was not affected by either UVR+PAR or PAR treatment (Fig. 2C). On the other hand, in the same post-exposure, dark incubations, the ^{35}S-DMS yield from dissolved DMSP consumption was always higher (4 to 8 % of the consumed ^{35}S-DMSP; $p < 0.05$, Tukey's test) after UVR+PAR treatment compared to the dark controls (2 to 4.6 %, Fig. 2D). The PAR treatment again had no effect on the ^{35}S-DMS yield, as its ratio to the dark control for all samples was approximately 100 %.

Effects of light intensity on ^{35}S-DMSPd consumption and ^{35}S-DMS yield. Sub-samples of freshly prepared 0.8-μm-filtered samples were exposed to 0, 18, 35, 57 or 100 % of the intensity of full spectrum solar radiation (i.e., UVR+PAR) for 5 h. Integrated doses of PAR, UVA and UVB for the 100 % intensity treatment are presented in Table 2 (August 30, 2002). The rate constant for ^{35}S-DMSPd consumption in post-exposure, dark incubations was progressively inhibited with higher light intensities (Fig. 3A). This pattern was similar to the pattern observed for ^{3}[H]-leucine incorporation rates, a general indicator of bacterial biomass production, suggesting strong inhibition of bacterial activity in samples exposed to higher intensities of solar radiation. The yield of ^{35}S-DMS, measured after 24 hr post-exposure, dark incubation was not affected by light intensities up to 60 % of surface irradiation, but yields were nearly two-fold higher in the 100 % intensity treatment compared to all other treatments and the 0 % (dark) control (Fig. 3B).

Mediterranean and Sargasso Sea UVR and PAR experiments

^{35}S-DMSP degradation and ^{35}S-DMS yield in the Mediterranean Sea. Degradation rate constants for ^{35}S-DMSPd consumption in the coastal Mediterranean Sea, with water from either the surface mixed layer (0.5 m, August 5, 2003) or below the mixed layer (5 m, August 7, 2003), were progressively inhibited (relative to dark samples) by exposure to a larger fraction of the total solar spectrum (UVR+PAR < UVA+PAR < PAR < Dark, Fig. 4A). Although the trends were the same, the rate constant for ^{35}S-DMSPd consumption in the dark control of the surface sample was approximately four-fold higher than the rate constant in the dark control of the 5 m water, and the amount of inhibition was about 70 % in the more active surface water, compared with only 30 % in the 5 m water (Fig. 4A).

While the rate constant was inhibited by solar light exposure in both waters samples we observed opposite patterns between the two water samples with respect to ^{35}S-DMS yield from ^{35}S-DMSPd consumption. The surface water (August 5, 2002) had the highest ^{35}S-DMS yield in the dark control, and yields decreased by > 30 % in light exposed samples. No differences between the light treatments were visible (Fig. 4B). In contrast, the ^{35}S-DMS yield in the subsurface sample from 5 m (August 7, 2002) showed the lowest yield in the dark control and progressively higher values in samples exposed to a larger fraction of the total solar spectrum (Fig. 4B).

Depth dependent ^{35}S-DMS yields from ^{35}S-DMSPd in the Sargasso Sea. On two occasions, unfiltered seawater collected from one depth in the upper mixed layer (0.5 m, April, 2002 and 10 m, July 2004) of the Sargasso Sea was incubated for 7–8 h on a free floating drifter array, which held samples at fixed depths in the euphotic zone. In the April 2002 deployment, the ^{35}S-DMS yield (in post-exposure, dark incubations) was lowest at the surface and increased with depth to yields at 20–30 m that were the same as ^{35}S-DMS yields in the dark control (Fig. 5A). The inhibition (relative to the dark controls) was about 36 % for surface-irradiated samples, and decreased in samples irradiated at deeper depths (Fig. 5A). A different pattern was observed in July, 2004. In this drifter deployment, the DMS yield was highest in the surface-irradiated samples by a factor of 1.8 compared to the dark control, with lower yields observed deeper in the water column, except for 5 m (Fig. 5B). In contrast, in both experiments, ^{3}[H]-

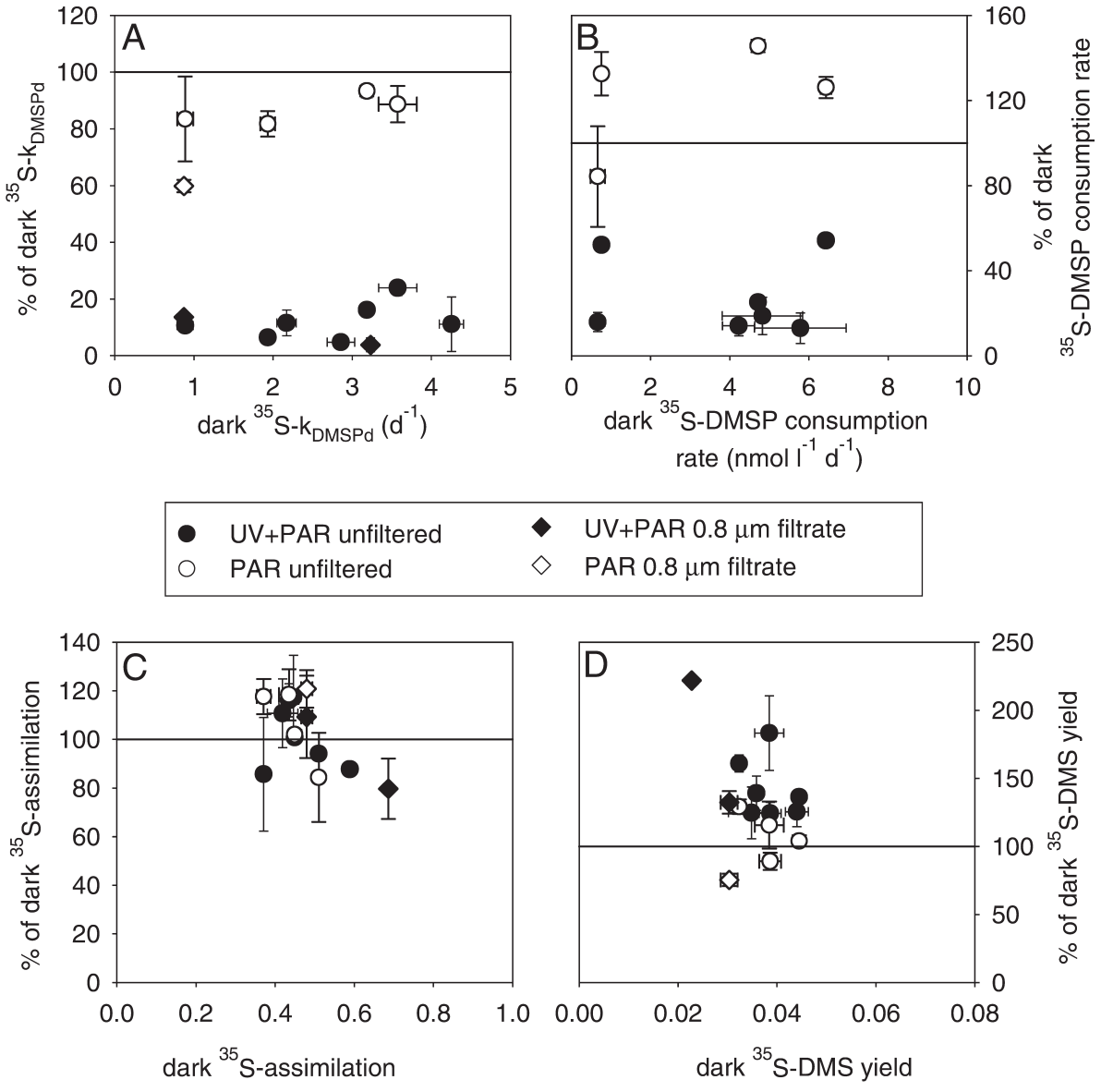

Figure 2. Effect of solar radiation on ^{35}S-DMSPd consumption and end product partitioning in 0.8 µm filtered and unfiltered water samples from the Gulf of Mexico, that were exposed to solar radiation, then incubated for 24 h in the dark with added ^{35}S-DMSPd (total of nine experiments; sample details are given in Table 1). For each panel, the percentage of the parameter (e.g. ^{35}S-DMS yield) in the light treatment (PAR or UVR+PAR) to that in the dark control is plotted as a function of the magnitude of the parameter obtained in the dark control. A) First order loss rate constant (^{35}S-k_{DMSPd}) of ^{35}S-DMSPd; B) ^{35}S-DMSPd consumption rate (0.8 µm filtered samples not determined); C) ^{35}S-DMSPd assimilation; and D) ^{35}S-DMS yield. Data represent individual water samples and are given as the mean of duplicate or triplicate incubations. Error bars represent the range of the data.

leucine incorporation rates were lowest in the surface irradiated samples and progressively increased at deeper irradiation depths to values similar to those in the dark controls (data not shown, Slezak et al., unpublished results).

DMS production from total versus dissolved DMSP in the Gulf of Mexico

Two experiments were carried out with Gulf of Mexico water (one from a coastal and one from a shelf site) in which we examined how DMS production rates from DMSPt compared to DMS production rates from DMSPd (calculated from the ^{35}S-DMSPd consumption multiplied by the fraction converted into ^{35}S-DMS) and whether solar radiation exerts any effects on the ratio between the two DMS sources. In both experiments, the dissolved ^{35}S-DMSPd consumption rate was always inhibited in treatments receiving UVR+PAR and the yield of ^{35}S-DMS from DMSPd increased in UVR+PAR treated samples as compared to the dark controls (^{35}S-data included in Fig. 2A, B and D).

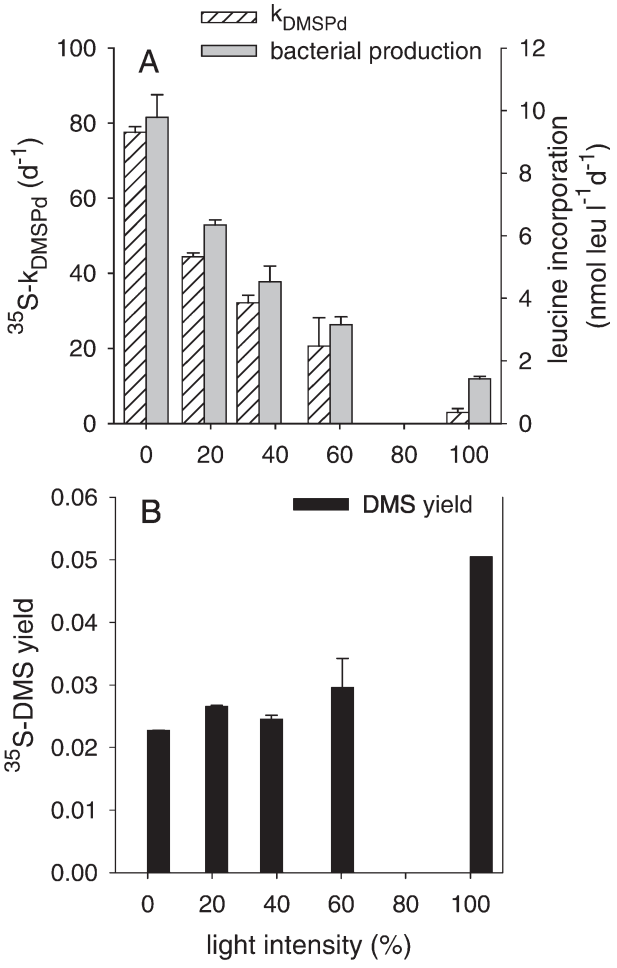

Figure 3. Effect of light intensity on the consumption of ^{35}S-DMSPd, bacterial biomass production and ^{35}S-DMS yield in 0.8 µm-filtered coastal surface water from the Gulf of Mexico after exposure to different light intensities by means of neutral density screens. A) ^{35}S-DMSPd rate constant and [^{3}H]-leucine incorporation rate, and B) ^{35}S-DMS yield. The seawater used in this study was collected on August 30, 2002. Values are given as the mean of duplicate samples, and error bars represent the range of the data.

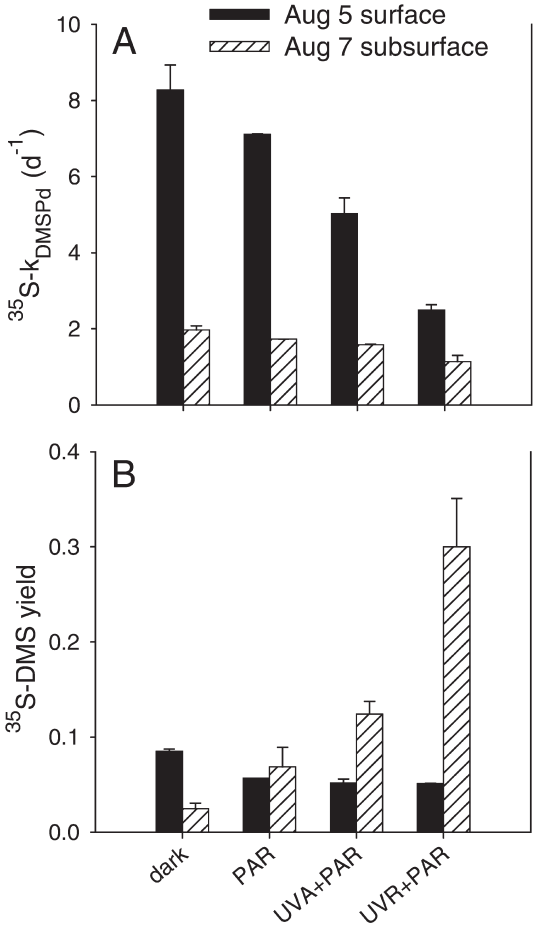

Figure 4. Effects of different spectral fractions of solar radiation on the consumption of ^{35}S-DMSPd and the yield of ^{35}S-DMS in surface water (0.5 m; August 5, 2004) and subsurface water (5 m, mixed layer at about 3 m; August 7, 2004) from the coastal Mediterranean Sea. Long-pass filters were used to attenuate specific spectral regions of the solar spectrum. A) DMSP consumption rate constant (^{35}S-k_{DMSPd}) and B) ^{35}S-DMS yield. Data denote the mean of duplicate incubations, and error bars the range of the data.

Exposure to solar radiation did not significantly affect DMS production rates from DMSPt in post-exposure, dark incubations. In both experiments, the ratio between DMS production from DMSPd to DMS production from DMSPt was always substantially less than 1 (Table 3). In the experiment with coastal water, the ratio between DMS production from DMSPd to DMS production from DMSPt decreased progressively from dark to PAR to UVR+PAR treatments (October 16, 2002; Table 3). In the shelf water sample, no differences between the light treatments were observed. Results from both experiments are indicative of a significant non-DMSPd-derived (i.e. non-bacterial) DMS source.

Discussion

On the production side of the processes controlling DMS concentrations in the upper oceans, the yield of DMS from consumed DMSP is believed to be crucial because it is known to vary from almost 0 to 100 % (Simó and Pedrós-Alió, 1999). The turnover rate of DMSP can be substantial (0.3 to almost 130 nM per day for dissolved DMSP (Kiene, 1996b; Ledyard and Dacey, 1996; Van Duyl et al., 1998); therefore, small variations in the DMS yield will result in considerable variations in the production of DMS in the upper ocean. For this reason, it is essential to understand the effect of solar radiation, particularly UVR, on the fate of degraded DMSP, as it pertains to the production of DMS in the photic zone.

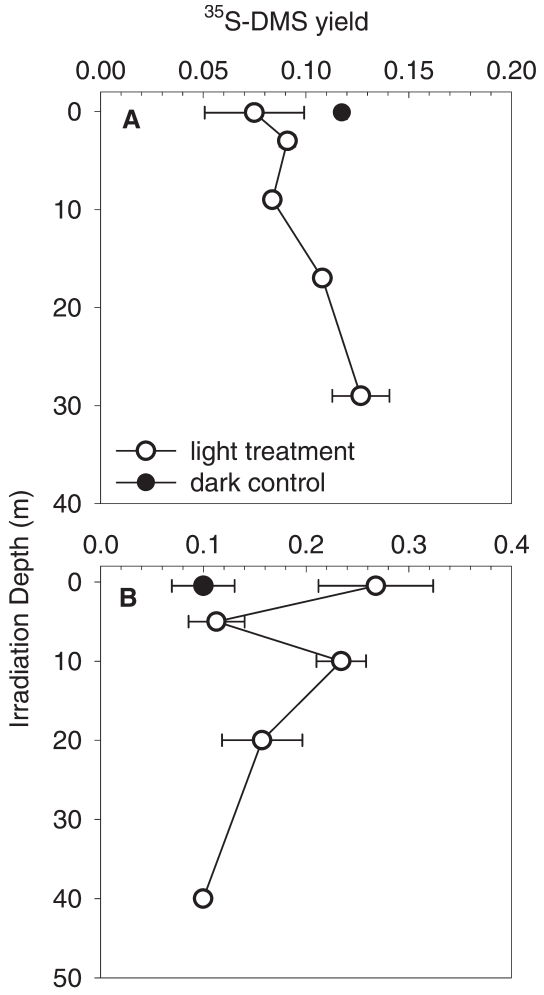

Figure 5. Effect of actinic solar radiation in the water column on the post irradiation, dark ^{35}S-DMS yield from DMSPd consumption in unfiltered water samples from the Sargasso Sea. For each drifter experiment, seawater was collected from one depth and exposed to *in situ* irradiance at different depths in the water column for 7–8 h. Water samples: A) 31° 30' N, 69° W, collected at 0630 on April 15, 2002 (sampling depth 0.5 m, mixed layer depth 21 m, 1 % PAR depth 100 m, 1 % $UVR_{315\,nm}$ depth 25 m) and B) 30° 29' N, 65° 05' W, collected at 0430 on July 17, 2004 (sampling depth 10 m, mixed layer depth 21 m, 1 % PAR depth 103–128 m, 1 % $UVR_{315\,nm}$ depth 37–40 m). Values denote the mean of duplicate samples, and error bars represent the data range.

Response of ^{35}S-DMS yield to solar radiation

We investigated the effect of solar radiation on the DMS yield from DMSPd. Our working hypothesis is that the reduced bacterial demand for DMSP-sulfur, due to partial inhibition of protein synthesis and bacterial growth by high solar light doses (mainly UVR) (Herndl et al., 1993; Aas et al., 1996; Sommaruga et al., 1997), will divert more DMSP to the cleavage degradation pathway, thereby increasing the DMS yield (Kiene et al., 2000). In coastal and shelf sites in the Gulf of Mexico, the high sulfur demand of the actively growing bacterial community resulted in rather high ^{35}S-DMSPd assimilation and very low ^{35}S-DMS yields (2–8%) in dark controls (Fig. 1 and 2, see also Kiene and Linn, 2000b). Whilst in the same waters, the UVR-induced inhibition of the initial ^{35}S-DMSPd assimilation rate (Fig. 1B) was consistently accompanied by a shift towards higher ^{35}S-DMS yields (Figs. 1–3). This finding supports our hypothesis that the reduced sulfur demand due to inhibition of bacterial activity diverts more DMSPd towards the cleavage pathway with more DMS production per unit of consumed DMSPd.

The picture becomes more complicated in less productive marine systems like the mesotrophic Mediterranean or oligotrophic Sargasso Sea. Results from two of the four experiments from these systems resulted in increased DMS yields with increasing exposure to UVR, consistent with the Gulf of Mexico findings. However, in the other two experiments, one from the Mediterranean Sea and one from the Sargasso Sea, the inhibition of bacterial activity and the likely, simultaneous reduction of the bacterial sulfur demand, in irradiated samples was not accompanied by a shift to higher ^{35}S-DMS yields, but rather to lower yields (and thus higher demethylation rates) (e.g., Fig. 4B—August 5, 2003). Variations in light doses between experiments from the same site were small and therefore not likely a cause for the opposite pattern that was observed for ^{35}S-DMS yields (Table 2; e.g., Mediterranean Sea).

Differences in the composition and physiological status of the microbial community might explain the opposite pattern in ^{35}S-DMS yields that we observed in two cases in response to exposure to UVR (Arrieta et al., 2000; Winter et al., 2001). In the Mediterranean Sea, the water column was only weakly stratified on August 5, 2002, whereas on August 7, 2002 an intrusion of cold water caused a more pronounced stratification (Sommaruga et al., 2005). Since water samples originated from the surface layer (0.5 m, August 5, 2002) and below the surface mixed layer (5 m, August 7, 2002), the microbial community composition and/or physiological status likely differed from each other and hence responded differently with respect to the ^{35}S-DMS yield. Consistent with our findings of higher DMSPd consumption rate constant in the 0.5 m water compared with the 5 m water, Alonso-Saez et al. (2006) found in the same two experiments that bacterial heterotrophic production was higher in the 0.5 m water. They also found that a) the response of the bulk bacterial heterotrophic production to UVR between the experiments was different as the 0.5 m community on Aug 5, 2002 was less sensitive (< 50 % inhibition compared to dark controls) than the 5 m community on Aug 7, 2002 ~80 % inhibition compared to dark controls) and that b) the inhibitory effects were not the same for all bacterial groups (*α-Proteo-*

Table 3. Effects of solar radiation on rates of DMS production from total and from dissolved DMSP in two different seawater samples from the Gulf of Mexico collected near Dauphin Island, Alabama. Rates were obtained during post-exposure, dark incubations, amended with DMDS, conducted after 6 h pre-incubations in the light. Statistical comparisons (student t-test) are based on regression slopes for DMS production from DMSPt. Error denotes ranges of the mean.

date	Light treatment	DMS production from DMSPt (nM h^{-1})	^{35}S-DMS production from DMSPd (nM h^{-1})	Ratio: DMS from DMSPd/ DMS from DMSPt
12-Sep 2002 shelf	dark control	0.098 ± 0.012	0.034 ± 0.002	0.35 ± 0.014
	PAR	0.061 ± 0.011	0.046 ± 0.005	0.75 ± 0.038
	UVR+PAR	0.074 ± 0.000	0.024 ± 0.001	0.32 ± 0.002
16-Oct 2002 coastal	dark control	0.034 ± 0.002	0.025 ± 0.007	0.74 ± 0.034
	PAR	0.059* ± 0.005	0.024 ± 0.003	0.41 ± 0.012
	UVR+PAR	0.034 ± 0.002	0.007 ± 0.001	0.21 ± 0.003

* significant different from dark control at $p < 0.05$ or higher

bacteria were more sensitive to UVR than β- and γ-*Proteobacteria*). In particular, within the α-*Proteobacteria,* members from the *Roseobacter* cluster were more resistant to UVR than members from the SAR11 cluster; both groups have representatives that consume DMSPd (Malmstrom et al., 2004a; 2004b; Vila et al., 2004). Further, the relative contribution of these two groups to the bulk bacterial community differed between the two experiments (Alonso-Saez et al., 2006). These observations may explain the differences that we observed in the response of the DMS yield to solar irradiation (Fig. 4).

It is likely that the different responses observed in DMS yields with depth in the Sargasso Sea (Fig. 5) are also due to physiological and/or phylogenetic differences in the microbial communities between the spring experiment in April 2002 and the summer experiment from July 2004, as the communities will likely differ throughout the seasonal cycle (Carlson et al., 1996; Fuhrman et al., 2006). During a cruise in the Ross Sea (Nov 2005) to investigate the early stages of a *Phaeocystis antarctica* bloom, we observed that the response of the DMS yield to solar radiation changed from increasing DMS yields with increasing UVR exposure during the pre-bloom, to decreasing yields with increasing UVR during the onset of the bloom (Toole, Slezak et al., unpublished results).

The use of surface solar radiation and 5–6 h exposure times places our results at the high end of responses that might be expected in the water column, since vertical mixing did not occur during our incubations. Mixing to deeper depths within the water column, and hence lower light levels, would tend to ameliorate the inhibitory effect of UVR on DMSPd degradation. Attenuation of the light intensity by either neutral density screens or exposure to the natural light field on *in situ* drifters, as performed in this study (Fig. 3 and 5), can provide a better estimate of how the effects that we observed might be extrapolated to the field, although these experiments still do not consider mixing. Changes in the ^{35}S-DMS yield with exposure to solar radiation will depend on a) the attenuation of solar irradiance in the water column (e.g. Kieber et al., 1997; Toole et al., 2006) and b) the mixing rate and depth (Herndl et al., 1998; Huot et al., 2000). In the highly productive, well mixed coastal environment, solar radiation is rapidly attenuated in the water column, and therefore microorganisms will be rapidly mixed down into UVR-shaded depths where they can recover from any radiation damage received during their transit time at the surface (Kaiser and Herndl, 1997). Hence, in systems such as the coastal Gulf of Mexico, the increased yield of DMS from DMSPd caused by solar radiation (Fig. 2) will likely be evident only at shallow depths. In mesotrophic and oligotrophic systems, especially during periods of shallow stratification, the upper water column is well illuminated with substantial levels of UVR and PAR (e.g., the 1 % light level for UVB_{315nm} was below the mixed layer depth in all experiments from the Mediterranean and Sargasso Sea, Figure 5, see also Sommaruga et al. (2005). Thus, in meso- and oligotrophic systems, the effect of solar radiation on DMS yields can be expected down to considerable depths in the upper water column (e.g., most of the surface mixed layer, Fig. 5).

Estimation of DMS production from DMSPd after solar irradiation

The ^{35}S-DMS yield was multiplied by the ^{35}S-DMSPd consumption rate (Kiene and Linn, 2000a) to estimate the DMS production from DMSPd in our samples, with and without UVR treatment (Table 4). The calculation is based on the assumption that the DMS yield from DMSPd is constant during the 24 h post-exposure, dark incubation. The validity of this assumption is supported by the time course results of ^{35}S-DMSP degradation, which demonstrated that the DMS yield was relatively constant during the 24 h dark incubation (Fig. 1E).

Table 4. DMS production rates (± ranges) calculated as the product of the ^{35}S-DMSPd consumption rates by the ^{35}S-DMS yields. Data for the Mediterranean Sea are not available due to suspect DMSPd concentrations and for the spring experiments from the Sargasso Sea due to missing ^{35}S-DMSPd consumption rate constants. N.D. = not determined.

	Irradiation depth (m)	^{35}S-DMS production rate (nmoles l^{-1} h^{-1})		
Date		dark	PAR	UVR+PAR
Gulf of Mexico				
7/23/2002	0	0.204 ± 0.063	N.D.	0.032 ± 0.014
8/7/2002	0	0.152 ± 0.015	N.D.	0.030 ± 0.012
8/9/2002	0	0.190 ± 0.023	N.D.	0.052 ± 0.025
8/21/2002	0	0.153 ± 0.006	0.287 ± 0.010	0.062 ± 0.005
8/30/2002	0	N.D.	N.D.	N.D.
9/5/2002	0	0.249 ± 0.016	0.276 ± 0.018	0.167 ± 0.005
9/12/2002	0	0.034 ± 0.002	0.046 ± 0.005	0.024 ± 0.001
10/16/2002	0	0.025 ± 0.007	0.024 ± 0.001	0.007 ± 0.001
		dark		Irradiated sample
Sargasso Sea				
7/17/2004	0	0.103 ± 0.023		0.030 ± 0.005
	5			0.034 ± 0.013
	10			0.032 ± 0.002
	20			0.056 ± 0.006
	40			0.033 ± 0.001

In the Gulf of Mexico, UVR caused a shift to higher DMS yields by, on average, a factor of 1.4 compared to dark controls (Fig. 2D), but simultaneously UVR reduced the DMSPd consumption by a factor of ~ 4 (Fig. 2B,) leading to an average ~ 3-fold decrease in the production of DMS from DMSPd in UVR irradiated samples (on average 0.05 nM h^{-1}) relative to the dark control (0.14 nM h^{-1}) (Table 4). Therefore, on a short term, the net effect of UVR in coastal and shelf waters of the Gulf of Mexico was a lower flux from DMSPd into the DMS pool. The DMS production rates in the present study compare well with previously estimated rates from shelf sites in the Gulf of Mexico (Kiene and Linn, 2000a). It should be noted that DMSPd consumption rates and hence the calculated DMS production rates here and in previous studies, could be overestimates because the recently introduced method of small volume drip filtration (SVDF) was not used for the determination of DMSPd concentrations (Kiene and Slezak, 2006). Future experiments using the SVDF method should provide a better estimation of the effects of UVR on the DMS production from DMSPd.

In oligotrophic systems, the simultaneous increase in DMS yield from DMSPd and decrease in DMSPd consumption rate may also offset each other or they may result in higher DMS production rates after UVR exposure. In the Sargasso Sea during summer 2004, the ^{35}S-DMS yield for the surface irradiated sample increased up to 2.6 fold compared to dark controls (Figure 5B), while the ^{35}S-DMSPd consumption rate decreased by 80 % (data not shown). The net effect was that ^{35}S-DMS production rates were on average 64 % lower in the irradiated samples compared to the dark control (Table 4), with no visible change at deeper exposure depths. In contrast, a 50 % reduction of ^{35}S-DMSPd consumption in the Mediterranean Sea (measured here as the rate constant only, Figure 4A; DMSPd concentrations were not available) accompanied by a 10-fold increase in ^{35}S-DMS yield is likely to result in a higher ^{35}S-DMS production rate.

This variable trend found in the Sargasso and Mediterranean waters may very well be the norm for cases where the ^{35}S-DMS yield increases with increasing UVR, as the sulfur demand for protein synthesis decreases paralleling the decrease in bacterial activity (Herndl et al., 1993; Aas et al., 1996; Sommaruga et al., 1997) and DMSPd consumption (Slezak et al., 2001). Conversely, when both, the ^{35}S-DMS yield and DMSPd consumption rate decrease with UVR exposure, then the ^{35}S-DMS production rate will decrease substantially. It is for this reason that we observed a large, 40 to 90 %, reduction of the DMS production rate in surface irradiated samples compared to dark controls in two samples (Fig. 4: August 5, 2003; Fig. 5A).

DMS production from a non-DMSPd source

Since in most cases the simultaneous inhibition of DMSPd consumption and increase of DMS yields upon UVR exposure led to a lower DMS production from DMSPd, we tested for a particulate DMSP-derived DMS production (e.g. from phytoplankton and/or micrograzers). In our two experiments, the ratio of DMS production from DMSPd to DMS production from DMSPt was always less than 1 for all

light treatments and dark controls (Table 3). Further, in the coastal water this ratio decreased in the PAR and UVR+PAR treatments compared to the dark controls, which points to a larger contribution of the non-bacterial community to the overall DMS production under solar radiation, although total DMS production was not affected by light (Table 3). Evidence for a non-bacterial DMS source was confirmed in the October 16, 2002 experiment by inhibiting DMSPd consumption in the UVR+PAR irradiated samples with 50 μM glycine betaine (GBT), a known inhibitor of this process (Kiene and Gerard, 1995) (data not shown). DMS continued to accumulate in the GBT amended samples even though ^{35}S-DMSPd consumption was inhibited by $>97\%$ (data not shown). These preliminary results certainly cannot be extrapolated to all regions, but they clearly provide evidence for a non-bacterial contribution to the DMS production of up to 80%. The fact that a substantial fraction of total DMS production came from a non-DMSPd source, and a larger fraction from the non-DMSPd source after UVR exposure in one experiment, supports the suggestion of significant DMS production from non-DMSPd sources in non-blooming plankton communities as suggested by Toole and Siegel (2004) and Simó and Pedrós-Alió (1999). While solar radiation had no substantial effect on DMS production from DMSPt in our limited tests (Table 3), this could be different in systems where the response of the non-bacterial DMS producers to solar radiation might be more pronounced. Further investigation of light effects on total DMS production is warranted.

Summary

In summary, we demonstrated that solar radiation, particularly UVR, often increases the DMS yield from DMSPd consumption. This finding, on its own, is consistent with empirical observations of higher summer concentrations of DMS when shallow mixed layers and high solar radiation doses are common in surface waters (Dacey et al., 1998; Simó and Pedrós-Alió, 1999; Toole et al., 2003). However, in the majority, our data also showed that the calculated DMS production rates (obtained from DMSPd consumption rates and DMS yields) actually decreased with exposure to solar radiation. The response to UVR is complex because of potential variations in the composition and physiological status of the microbial consortia. In two preliminary experiments with seawater samples from the Gulf of Mexico, we provided evidence for an, at times, substantial non-bacterial DMS production. The present data set adds new information on how solar radiation affects DMS production but they do not allow for predictions on a large scale; more studies in a variety of systems as well as on longer time scales are needed to help understand the diversity of responses of the DMS(P) dynamics to UVR.

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