

## Light-stimulated production of dissolved DMSO by a particle-associated process in the Ross Sea, Antarctica

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### *Abstract*

Dimethylsulfoxide (DMSO) is an abundant form of methylated sulfur in marine systems and it is known to be produced from dimethylsulfide (DMS). Using radiolabeled  $^{35}\text{S}$ -DMS and gas chromatography techniques, we quantified the dissolved DMSO (DMSOd) produced from photo- and biological oxidation of dissolved DMS and compared the DMSOd production from these pathways with the net change in DMSOd concentrations in unfiltered seawater samples. The net change in DMSOd in light-exposed treatments exceeded DMSOd production from photo- plus biological oxidation of dissolved DMS. This indicated that DMSOd was produced by one or more light-driven processes likely associated with particulate material. Results from in situ incubation arrays showed that the relative importance of DMSOd production processes was dependent on irradiation depth, with the unidentified particle-associated process and dissolved DMS photooxidation the main DMSOd sources close to the surface (0–10 m) and biological oxidation of dissolved DMS the main process at depths at which the light level was low (>10 m). Deckboard and in situ incubations revealed that DMSOd production from the particle-associated process was stimulated by ultraviolet radiation. Higher particle-associated production of DMSOd in samples more prone to suffer light-induced stress supports the hypothesis that this process was related to phytoplanktonic biosynthesis and release of DMSO because of oxidative stress. Our results suggest that particle-associated DMSOd production is an important source of DMSOd in surface waters of the Ross Sea and also help to explain why DMSOd is periodically the main organosulfur compound detected in the upper water column.

Dimethylsulfoxide (DMSO) is involved in the global sulfur cycle, in both the atmosphere (Koga and Tanaka 1993) and the oceans (Lee and de Mora 1999). DMSO in the ocean is produced from the oxidation of dimethylsulfide (DMS), a biogenic sulfur-containing gas that is produced from the cleavage of dimethylsulfoniopropionate (DMSP), which is synthesized by a variety of marine phytoplankton (Keller et al. 1989). Considerable attention

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has been directed to the study of DMS and its precursor, in part because of the hypothesized role of DMS in a self-regulated feedback mechanism between phytoplankton and climate (Charlson et al. 1987). In contrast to the intensive research on DMS and DMSP, much less attention has been paid to the study of DMSO. Methodological shortcomings prevented accurate quantification of DMSO in seawater until relatively recently (Hatton et al. 1994; Kiene and Gerard 1994; Simó et al. 1996), but now it is recognized that dissolved DMSO can represent a significant fraction of the dissolved dimethylsulfur pool, periodically exceeding DMS or DMSP concentrations (Hatton et al. 1996; Lee and De Mora 1996; Simó et al. 1997). DMSO concentrations have been measured in a variety of environments (Hatton et al. 2004), yet relatively little is known about the sources and sinks of this compound in the ocean and its interactions with the DMS pool.

Bacteria capable of reducing DMSO to DMS have been isolated from seawater (González et al. 1999). Therefore, this process might be an alternative pathway for DMS production that could affect seawater DMS concentrations and thus its capacity to exchange to the atmosphere. Bacteria have also been proposed to oxidize DMS to

DMSO on the basis of the ability of several aerobically grown cultures to carry out this process (Zhang et al. 1991; Juliette et al. 1993). Recently, del Valle et al. (2007) showed that biological oxidation of DMS to DMSO occurred in the water column of the Sargasso Sea, with higher conversion efficiencies in the surface mixed layer compared with deeper depths. Dissolved DMSO (DMSO<sub>d</sub>) can also be produced from photooxidation of DMS, mediated primarily by ultraviolet (UV) radiation in the presence of photosensitizers (Brimblecombe and Shooter 1986; Kieber et al. 1996; Toole et al. 2003). Wet deposition of DMSO from the atmosphere constitutes another potential source of DMSO<sub>d</sub> to surface waters (Kiene and Gerard 1994; Ridgeway et al. 1992), although this process is not an important contributor to the marine sulfur cycle (Sciare et al. 1998).

The presence of particulate DMSO in seawater has been attributed to phytoplankton production because different phytoplankton species have been shown to biosynthesize DMSO in culture (Simó et al. 1998). It has been suggested that DMSO leakage from algal cells might also contribute to the dissolved pool (Simó et al. 2000), but this has not been directly observed or quantified in a natural system. Because DMSO is membrane permeable (Liu et al. 1997), it can potentially diffuse out of the cell, or it might be released into the dissolved pool by the same mechanisms that contribute to cellular DMSP release (e.g., zooplankton grazing) (Lee et al. 2003).

In this work we documented the production of DMSO<sub>d</sub> by a particle-associated process in the Ross Sea, Antarctica, an area known to have high concentrations of DMSP and DMS during the austral spring and summer. We studied the effects of solar radiation on DMSO<sub>d</sub> production from a particle-associated process as well as from photo- and biological oxidation of dissolved DMS. We found that the particle-associated DMSO<sub>d</sub> production is driven mainly by UV radiation and that it is an important source of DMSO<sub>d</sub> in surface waters of the Ross Sea.

## Methods

**Study area**—Seawater samples were collected aboard the RVIB *Nathaniel B. Palmer* during two oceanographic cruises to the Ross Sea, Antarctica, in Jan and Nov 05. Seawater for the different experiments was collected in Niskin bottles attached to a CTD rosette at different hydrographic stations (Fig. 1).

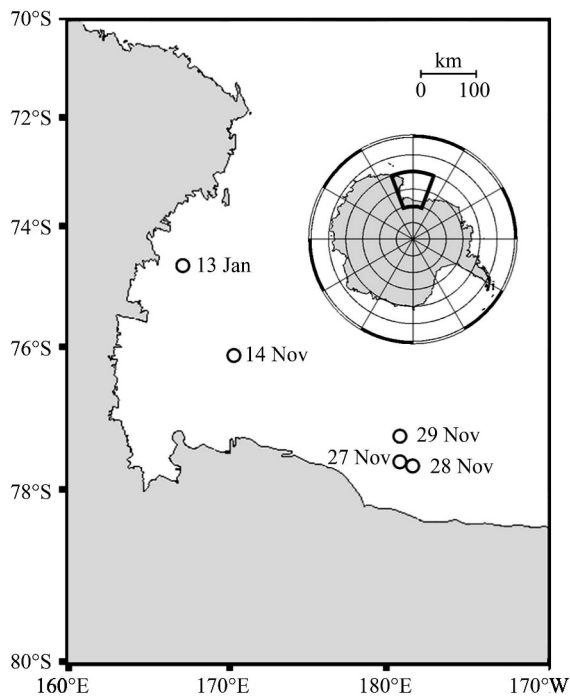


Fig. 1. Map showing the geographical locations within the Ross Sea where water was collected for the different experiments. Dates shown correspond to the year 2005.

**Experimental design**—A series of in situ and deckboard incubation experiments were conducted to test for the effects of solar radiation on the relative importance of DMSO<sub>d</sub> production pathways. Although the location of sample collection (Fig. 1) and the incubation conditions (e.g., incubation time, light dose) varied for the different experiments (see below), the general experimental design was the same. Seawater samples were dispensed into different acid-cleaned Teflon bottles or quartz tubes, and duplicate containers were allocated to different treatments (Table 1), except where otherwise noted.

The different treatments allowed the direct quantification of DMSO<sub>d</sub> production from dissolved DMS photooxidation (DMSO<sub>ph</sub>, treatment A), the indirect quantification of DMSO<sub>d</sub> production from the biological oxidation of dissolved DMS (DMSO<sub>bo</sub>, Eq. 1), and the net change in DMSO<sub>d</sub> concentration (DMSO<sub>net</sub>, treatment C). The difference between DMSO<sub>net</sub> and DMSO<sub>ph+bo</sub> (treatment C minus B, Table 1) represents the amount of DMSO<sub>d</sub> produced by processes other than photo- or biological

Table 1. Different treatments used in deck and in situ incubations to determine the production of DMSO<sub>d</sub> via the different production processes. Seawater samples used in treatments A and B were placed in 30- or 10-mL Teflon bottles. Treatment C samples were placed in 500-mL Teflon bottles. Quartz tubes were only employed in the in situ incubation carried out in Jan 05; 15-mL quartz tubes were used in treatment A and B, whereas 80-mL quartz tubes were utilized in treatment C.

Treatment	Added <sup>35</sup> S-DMS	Process quantified
A	0.2- $\mu$ m filtered seawater	DMSO <sub>d</sub> from DMS photooxidation (DMSO <sub>ph</sub> )
B	Unfiltered seawater	DMSO <sub>d</sub> from photooxidation and biological DMS oxidation (DMSO <sub>ph+bo</sub> )
C	Unfiltered seawater	net DMSO <sub>d</sub> concentration change (DMSO <sub>net</sub> )

oxidation of dissolved DMS ( $\text{DMSO}_{\text{extra}}$ , Eq. 2). The errors in the calculation of DMSO<sub>d</sub> produced in Eqs. 1 and 2 were propagated from errors on the direct measurements (i.e.,  $\text{DMSO}_{\text{ph+bo}}$ ,  $\text{DMSO}_{\text{ph}}$ , and  $\text{DMSO}_{\text{net}}$ ).

$$\text{DMSO}_{\text{bo}} = \text{DMSO}_{\text{ph+bo}} - \text{DMSO}_{\text{ph}} \quad (1)$$

$$\text{DMSO}_{\text{extra}} = \text{DMSO}_{\text{net}} - \text{DMSO}_{\text{ph+bo}} \quad (2)$$

*Effect of in situ light field on DMSO<sub>d</sub> production*—Two in situ incubation experiments were conducted. One experiment was carried out on 28 Nov 05 with seawater collected from 5 m, which was then incubated at fixed depths (2, 5, 10, and 15 m) for 25 h. The other in situ incubation experiment was carried out on 13 Jan 05 with water collected from 15 m and incubated at 0, 2, 5, 9, and 15 m for 7.1 h. Both in situ incubations were started in the morning (~08:30 h local time) with water collected 1 h before deployment. A series of duplicate sealed Teflon bottles (Nov) or quartz tubes (Jan) representing treatments A, B, and C (Table 1) were incubated at each depth and also in a dark incubator located on deck (dark control) with surface-running seawater to maintain in situ temperature ( $-1.8^{\circ}\text{C}$ ). Teflon bottles or quartz tubes were suspended in the water column beneath a free-floating buoy. This approach allowed the same water sample (i.e., seawater from 5 m in Nov and from 15 m in Jan) to be exposed to the natural light field corresponding to the different depths at which they were incubated. The mixed layer depth in the corresponding day of the experiment was located at 70 and 21 m in Nov and Jan, respectively. Thus, the floating arrays were entirely within the mixed layer in both experiments.

*Deck incubations*—A deck experiment was carried out on 27 Nov 05 with water from 20 m that was exposed to (1) full-spectrum solar radiation (photosynthetically active radiation [PAR] + ultraviolet A [UVA] + ultraviolet B [UVB]), (2) PAR + UVA, (3) PAR only, or (4) no light (i.e., dark) for 9 h starting at 08:45 h local time. For this experiment, treatments A, B, and C (Table 1) were carried out in triplicate. The PAR + UVA and the PAR-only treatments were obtained with the use of a Mylar Dfilm bag (~317-nm cutoff) and a Plexiglas UF3 box (~400-nm cutoff), respectively. Additional deck experiments were conducted with water collected from different depths and exposed to full-spectrum solar radiation on 14 Nov and 29 Nov 05. For the 14 Nov experiment, seawater was collected from 2, 20, 30, and 50 m and incubated on deck for 5 h. For the experiment carried out on 29 Nov, seawater collected from 2, 10, 20, and 50 m was incubated for 6 h. Both experiments were started at 09:00 h local time. All samples were incubated in water baths located on the ship's upper deck and kept at a constant temperature with running surface seawater ( $-1.8^{\circ}\text{C}$ ). All deck incubations were covered with neutral-density screen to reduce the incident solar radiation by 68%.

*Analytical procedures*—Determination of DMSO<sub>d</sub> production:  $^{35}\text{S}$ -DMS was added to samples at tracer levels

(~3.5 pmol L<sup>-1</sup>), and incubations were started just after the addition. Once the incubation was over, the total  $^{35}\text{S}$  activity in solution ( $A_{\text{TOT}}$ ) was quantified, as well as the nonvolatile (NV) activity present after removing the unreacted  $^{35}\text{S}$ -DMS by sparging for 10 min with N<sub>2</sub> ( $A_{\text{NV}}$ ). A subsample of the NV reaction products that remained in solution was treated with cobalt-doped NaBH<sub>4</sub> (Sigma) to reduce  $^{35}\text{S}$ -DMSO to volatile  $^{35}\text{S}$ -DMS (Simó et al. 1998, Riseman and DiTullio 2004), which was then removed by sparging. The remaining activity in the NV fraction after  $^{35}\text{S}$ -DMSO removal was quantified ( $A_{\text{NV-DMSO}}$ ). For more details on the analytical procedure, see del Valle et al. (2007).

The amount of DMSO<sub>d</sub> produced from DMS during the incubation time in treatment A ( $\text{DMSO}_{\text{ph}}$ , Table 1) and B ( $\text{DMSO}_{\text{ph+bo}}$ , Table 1) was calculated with the use of the following equation:

$$\begin{aligned} & \text{DMSO}_{\text{ph}} \text{ or } \text{DMSO}_{\text{ph+bo}} (\text{nmol L}^{-1}) \\ & = [\text{DMS}] \times \left( A_{\text{NV}}/A_{\text{TOT}} \right) \times \left( 1 - A_{\text{NV-DMSO}}/A_{\text{NV}} \right) \quad (3) \end{aligned}$$

where [DMS] is the concentration of DMS (nmol L<sup>-1</sup>) at the beginning of the incubation, and activities ( $A_{\text{TOT}}$ ,  $A_{\text{NV}}$ , and  $A_{\text{NV-DMSO}}$ ) are given in disintegrations per minute per milliliter (dpm mL<sup>-1</sup>). The first two factors of Eq. 3 represent DMS (nmol L<sup>-1</sup>) lost during the incubation as determined by the tracer approach. The third factor in Eq. 3 represents the fraction of the total  $^{35}\text{S}$ -DMS photochemically or biologically oxidized to  $^{35}\text{S}$ -DMSO<sub>d</sub> (i.e., DMSO yield).

The net change in DMSO<sub>d</sub> concentration in treatment C ( $\text{DMSO}_{\text{net}}$ ) was taken as the difference between DMSO<sub>d</sub> concentrations determined by gas chromatography (GC) at the beginning and end of the incubation.

*DMSO, DMS, and DMSP concentrations*: To determine DMSO<sub>d</sub> concentrations, 1–3-mL subsamples of GF/F (Whatman, muffled) drip-filtered seawater, obtained by procedures similar to those described in Kiene and Slezak (2006), were sparged for 10 min with N<sub>2</sub> (100 mL min<sup>-1</sup>) to remove any DMS that was initially present. When samples could not be run immediately, they were stored, after sparging, in closed vials at  $-20^{\circ}\text{C}$  and resparged immediately before analysis. DMSO was quantitatively reduced to DMS by the titanium chloride reduction method (Kiene and Gerard 1994). The DMS formed was cryotrapped and then analyzed on a Shimadzu GC-14 gas chromatograph containing a Chromosil 330 column and flame photometric detector (Kiene and Service 1991). Sampling for DMS was carried out by prescreening the sample directly from the Niskin bottle through a 20- $\mu\text{m}$  Nitex mesh to remove large phytoplankton cells and *Phaeocystis antarctica* colonies. The omission of this processing step produced artificially high DMS concentrations that were not reproducible. Screened seawater was collected into a 60-mL Teflon bottle, avoiding turbulence and letting the sample overflow the Teflon bottle. All samples for DMS concentrations were analyzed within 30 min of collection. The 20- $\mu\text{m}$  screened sample was syringe filtered through a GF/F filter into a sparge vial connected

Table 2. Average concentrations of DMS, dissolved DMSO (DMSOd), dissolved DMSP (DMSPd), total DMSP (DMSPt), and Chl *a* in the surface mixed layer determined at the different hydrographic stations sampled for this study in the Ross Sea.

Date	Latitude	Longitude	DMS (nmol L <sup>-1</sup> )	DMSOd (nmol L <sup>-1</sup> )	DMSPd (nmol L <sup>-1</sup> )	DMSPt (nmol L <sup>-1</sup> )	Chl <i>a</i> (μg L <sup>-1</sup> )
13 Jan 05	74°40'S	167°00'E	18.1	43.7	1.3	68.8	2.6
14 Nov 05	76°05'S	170°16'E	1.6	0.6	0.7	10.1	0.8
27 Nov 05	77°38'S	179°26'W	67.2*	39.2*	NA	NA	6.5*
28 Nov 05	77°39'S	178°38'W	39.5†	25.0†	NA	NA	5.5†
29 Nov 05	77°15'S	179°15'W	39.4	32.0	4.3	28.6	5.5

NA, data not available.

\* Values from one 20-m sample.

† Values from one 5-m sample.

directly to the cryotrapping system. The water sample was sparged with ultrapure helium and the cryotrapped DMS was analyzed on a Shimadzu GC-14 gas chromatograph. DMSPd samples were collected following the analytical procedures described in Kiene and Slezak (2006). Briefly, seawater was gravity filtered through a 47-mm GF/F glass filter, and the first 3.5 mL of filtrate was collected in a centrifuge tube containing 50 μL of 20% H<sub>2</sub>SO<sub>4</sub> to preserve DMSP and oxidize DMS. To determine total DMSP concentration (DMSPt), whole seawater was collected in 1-L Nalgene bottles containing 5 mL of 20% H<sub>2</sub>SO<sub>4</sub>. After >24 h, 1-mL subsamples for DMSPt and 3.2-mL samples for DMSPd were pipetted into glass vials, and 1 mL of 5 mol L<sup>-1</sup> NaOH was added to cleave the DMSP to DMS (and acrylate), which was then cryotrapped and detected by gas chromatography.

Chlorophyll *a* (Chl *a*) concentration and Fv:Fm ratio: Samples for Chl *a* analysis were filtered through AE filters applying a gentle vacuum (<5 mm Hg). Chl *a* extraction in 90% acetone was carried out at -20°C for 24 h. Fluorescence was measured with a TD-700 fluorometer (Turner Designs). The chlorophyll fluorescence parameter Fv:Fm was measured with a pulse amplitude modulation (PAM)-control fluorometer (Walz) after keeping the samples in the dark for 30 min once the experimental incubation was over.

Light dose measurements: The UV light dose experienced by the samples that were incubated in situ or in deck experiments was monitored by the use of chemical light meters (actinometers; Kieber et al. 2007). The UVA (320–400 nm) band was monitored by a nitrite actinometer (325–380 nm), and the UVB (290–320 nm) band was monitored by a nitrate actinometer (308–330 nm) (Kieber et al. 2007). Actinometry solutions were placed in 11-mL Qorpak vials, and the vials were exposed to the same incubation conditions as the treatment Teflon bottles or quartz tubes. The light dose obtained employing this approach represented the light dose reaching the outside of the incubation container. After the cruise, we determined that water samples contained in Teflon bottles receive 100% of the UVA dose and 88% of the UVB dose compared with samples contained in quartz tubes (data not shown). Thus, the difference in light transmission between incubation containers was relatively small, and the results from experiments with either quartz tubes or Teflon bottles should be comparable. Profiles of surface

percentage PAR and 320-nm radiation with depth were determined from vertical profiles of the downwelling irradiance determined with a PUV-511 profiling radiometer (Biospherical).

## Results

*Characteristics of the study site*—The geographic location of the stations sampled for the different experiments, as well as mixed layer average DMS, DMSOd, DMSPd, DMSPt, and Chl *a* concentrations are given in Table 2. During Nov 05, after the Ross Sea polynya opened, the phytoplankton assemblage was dominated by colonial *P. antarctica*, whereas during Jan 05, the phytoplankton community comprised mostly a mix of *antarctica* and a small pennate diatom, *Pseudonitzschia subcurvata* (Deneb Karentz pers. comm.).

*In situ drifter arrays*—In these experiments, seawater collected from one depth in the surface mixed layer was exposed to the natural light field at different depths in the water column of the Ross Sea. Time integrated light doses experienced by the incubated samples in the UVA and UVB spectral regions are shown in Table 3. In samples incubated at shallower depths, the net amount of DMSOd that accumulated in the samples (treatment C, DMSO<sub>net</sub>) exceeded the amount produced from the photochemical and biological oxidation of dissolved DMS (treatment B, DMSO<sub>ph+bo</sub>) (Fig. 2), suggesting the existence of at least one other process involved in DMSOd production. DMSOd production estimates from dissolved DMS determined with the use of either <sup>35</sup>S-DMS or net changes in DMSOd concentration measured by gas chromatography showed excellent agreement ( $p < 0.01$ ) when applied in 0.2-μm filtered water exposed to full-spectrum solar radiation. This suggested that the additional DMSOd production measured in the whole-water incubations was associated with particulate material because, in the absence of particles, no extra DMSOd production was detected.

The net amount of DMSOd produced in the different processes, as well as the relative importance of each process, varied as a function of the incubation depth and therefore of the experienced light spectrum and dosage (Fig. 2). In the array carried out in the spring, on 28 Nov 05 (Fig. 2a), photooxidation and the unidentified particle-

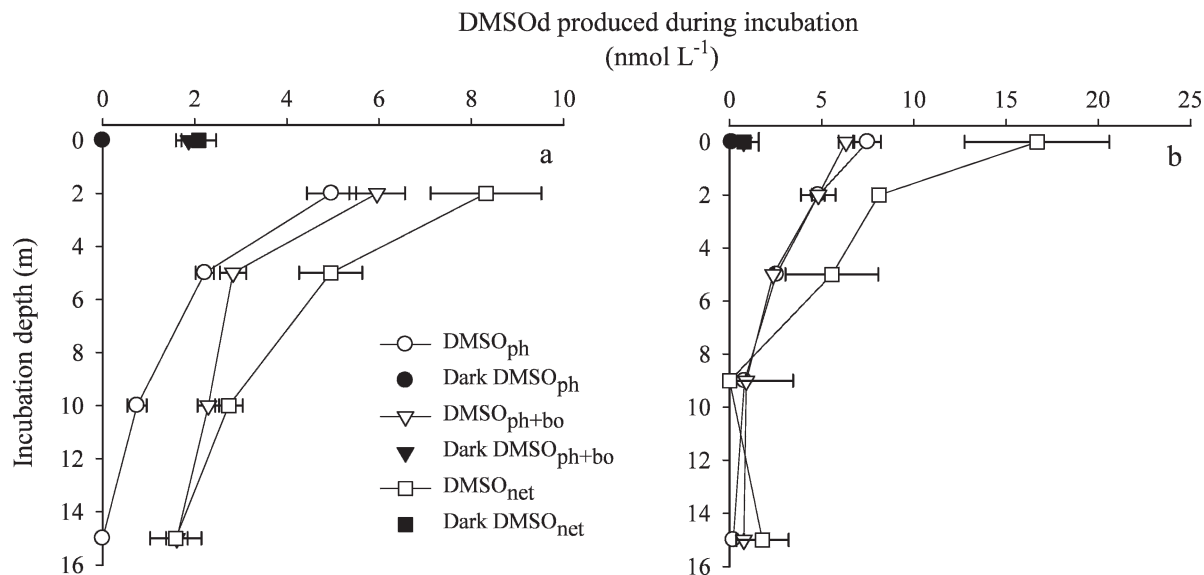


Fig. 2. In situ incubation arrays carried out during (a) Nov and (b) Jan 05. Seawater used in the incubations was collected from one depth in the surface mixed layer and subsequently exposed to natural light fields in the water column. Graphs show the DMSOd produced ( $\text{nmol L}^{-1}$ ) during the incubation time at each incubation depth (m) because of DMS photooxidation (treatment A,  $\text{DMSO}_{\text{ph}}$ ), DMS photo- and biological oxidation (treatment B,  $\text{DMSO}_{\text{ph+bo}}$ ), and the net change in DMSOd concentration (treatment C,  $\text{DMSO}_{\text{net}}$ ). Open symbols represent light-incubated samples; closed symbols represent dark controls. Horizontal bars denote the range from duplicate measurements.

associated process together contributed 88% of the net DMSOd production at both 2- and 5-m exposure depths. Production from photooxidation decreased exponentially with exposure depth ( $r^2 = 0.99$ ). DMSOd production from the unidentified process ( $\text{DMSO}_{\text{extra}}$ ) also decreased with depth, with the highest values observed in samples incubated at 2 and 5 m and no significant production seen at 15 m (Fig. 3a). The difference between  $\text{DMSO}_{\text{ph+bo}}$  and  $\text{DMSO}_{\text{ph}}$  appeared to be smaller at shallower incubation depths (i.e., 2 and 5 m), which would imply lower DMSOd production rates from biological DMS oxidation; however, this difference was not statistically significant in this experiment. Samples incubated at 15 m showed essentially the same behavior as the dark controls for all treatments, in agreement with the low solar light flux (especially UV) estimated for this depth (Table 3; Fig. 3). In the sample incubated at 5 m (i.e., at the depth from which the water was taken),  $5.0 \text{ nmol L}^{-1}$  DMSOd was produced in the 25-h incubation, which was equivalent to 20% of the initial DMSOd present at that depth (Table 2). When the values obtained were integrated from 2 to 15 m depth, DMSOd production from dissolved DMS photo- and biological oxidation, and the particle-associated process were  $0.80$ ,  $0.57$ , and  $0.63 \mu\text{mol m}^{-2} \text{ h}^{-1}$ , respectively. Therefore, by this approach, in the top 15 m of the water column, photooxidation was the main DMSOd-producing process (40.1%), followed by particle-associated DMSOd production (31.4%), and biological DMS oxidation (28.5%).

In the array carried out in summer (Jan 05), the amount of DMSOd produced by DMS photo- plus biological oxidation ( $\text{DMSO}_{\text{ph+bo}}$ ) was significantly higher than the amount produced by DMS photooxidation alone ( $\text{DMSO}_{\text{ph}}$ ) in the samples incubated at 9 and 15 m, as well

as in the dark controls (Fig. 2b). This implies significant biological oxidation of DMS in those samples. For the samples incubated at 0, 2, and 5 m, biological DMS oxidation could not be resolved from the difference between these two measurements, suggesting it was very

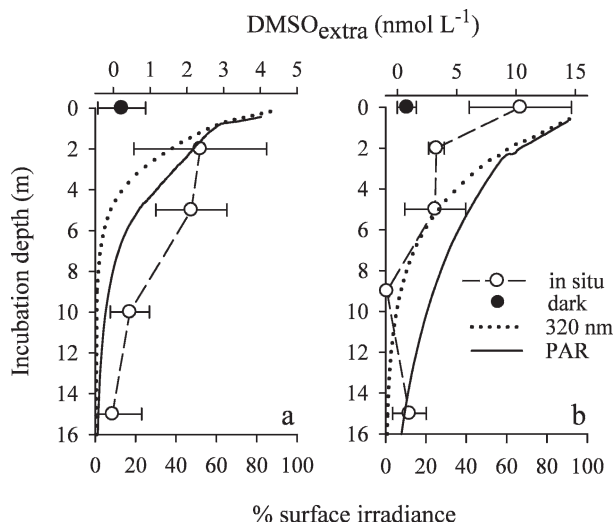


Fig. 3. Production of DMSOd from the unidentified particle-associated process ( $\text{DMSO}_{\text{extra}}$ ) in the in situ incubation arrays carried out during (a) Nov and (b) Jan in the Ross Sea (open circles). The filled circles are the production from this process in the dark controls. Error bars denote the propagated error from the difference between  $\text{DMSO}_{\text{net}}$  and  $\text{DMSO}_{\text{ph+bo}}$ . Dotted and solid lines in panels a and b show the percentage of surface irradiance at depth for 320 nm and PAR, respectively. All samples were incubated in the euphotic zone.

Table 3. Time-integrated light dose during in situ and deck incubations carried out during this study as determined by nitrate (308–330 nm) and nitrite (325–380 nm) actinometry (Kieber et al. 2007). The data for the deck experiment carried out on 27 Nov correspond to the light dose experienced on the full-spectrum treatment.

Date	Incubated depth (m)	Light dose ( $\mu\text{mol quanta cm}^{-2}$ )*		
		325–380 nm	308–330 nm	
In situ arrays	28 Nov†	2	47.8	15.14
		5	34.4	2.16
	10	2.6	BDL	
	15	0.2	BDL	
	13 Jan‡	0	193.0	18.90
Deck experiments	27 Nov†	2	66.4	8.73
		5	23.7	2.46
		9	3.6	0.54
		15	1.4	0.08
14 Nov†	—	29.7	3.48	
29 Nov†	—	104.0	16.23	

\* BLD, below detection limit. The detection limit (DL) for the high-performance liquid chromatography (HPLC) technique is  $\sim 0.013$  and  $0.008 \mu\text{mol quanta cm}^{-2}$  for the nitrite and nitrate actinometers, respectively. For the spectrofluorometric technique, the DL is 0.13 and  $0.08 \mu\text{mol quanta cm}^{-2}$  for the nitrite and nitrate actinometers, respectively.

† Light dose determined by spectrofluorometry.

‡ Light dose determined by HPLC.

low in these near-surface irradiated samples. When biological DMS transformation rates were measured in dark-incubated samples that had previously been exposed to light in the in situ array, strong inhibition of this process was evident in the samples that had been incubated at 0 and 2 m (Kieber et al. 2007). Therefore, inhibition of DMSOD production from biological DMS transformation in near-surface waters, together with an already low uninhibited DMSOD production from this process ( $0.77 \text{ nmol L}^{-1}$  in 9-h incubation, dark control), was responsible for the lack of significant differences between  $\text{DMSO}_{\text{ph+bo}}$  and  $\text{DMSO}_{\text{ph}}$  in near-surface-incubated samples. As expected, photochemical DMSOD production from dissolved DMS decreased exponentially with depth ( $r^2 = 0.95$ ) and was not significantly different from the dark control at 15 m (Fig. 2b). As with the array carried out in Nov, the net change in DMSOD concentration exceeded DMSOD production from photo- and biological oxidation of dissolved DMS in near-surface waters, indicating that the particle-associated process was stimulated by exposure to solar radiation (Fig. 3b). Moreover, no significant production from this process was observed in samples incubated at 9 and 15 m. Integration of the DMSOD production rates from photooxidation and the unidentified process over the top 15 m, yielded values of  $4.7$  and  $4.0 \mu\text{mol m}^{-2} \text{ h}^{-1}$ , respectively. Integrated DMSOD production from the biological oxidation of DMS was  $0.7 \mu\text{mol m}^{-2} \text{ h}^{-1}$ , as determined from postexposure incubations (Kieber et al. 2007) and assuming a DMSO yield of 28% for this process (obtained in the dark control for  $\text{DMSO}_{\text{ph+bo}}$ ). Therefore,

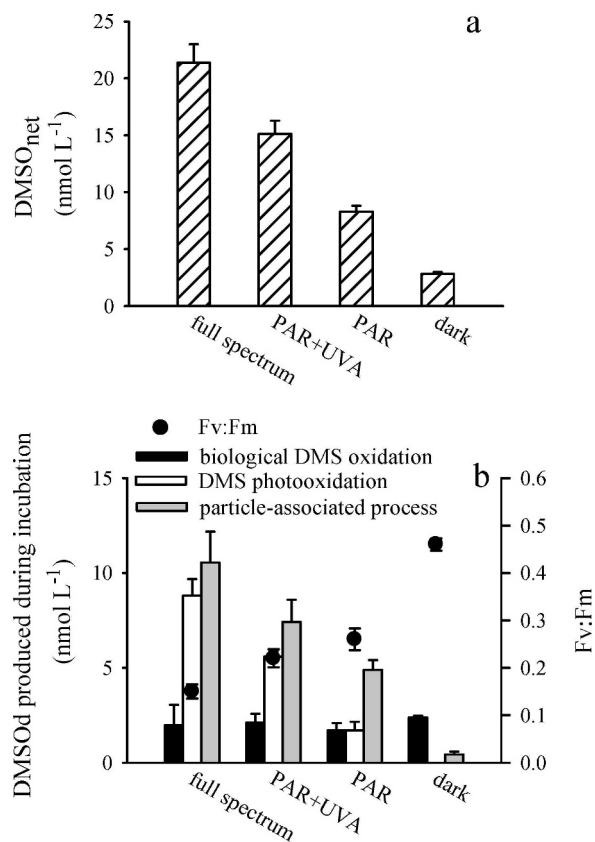


Fig. 4. Exposure of 20-m seawater to four different solar radiation treatments: full-spectrum solar radiation (UV + PAR), PAR + UVA, PAR only, and dark. (a) Net change in dissolved DMSO concentration ( $\text{DMSO}_{\text{net}}$ ) during incubation. (b) DMSOD produced by biological oxidation of dissolved DMS, photooxidation of dissolved DMS, and the particle-associated process under the four different light treatments. Filled circles represent the Fv:Fm ratio measured in the samples half an hour after the incubation was over. Vertical bars represent the calculated standard deviation of the mean of triplicate measurements.

DMSOD production from dissolved DMS photooxidation and the particle-associated process accounted for 49.8% and 42.6%, respectively, of the net change in DMSOD concentration over the top 15 m, with biological DMS oxidation contributing only 7.6%.

*Deck incubations*—DMSOD production under different light spectrum regimes: A deck incubation was carried out on 27 Nov 05 to evaluate the contribution of different spectral regions of solar radiation in the production of DMSOD. DMSOD net production was highest when the unfiltered seawater was exposed to full spectrum solar radiation (Fig. 4a). By selectively removing UVB or UVB + UVA and all light, we calculated that UVB, UVA, and PAR were responsible for 29%, 32%, and 26% of the net full-spectrum DMSOD production, respectively, whereas only 12% of the production was in the dark.

In all light-exposed treatments, the particle-associated process was the most important source of DMSOD, and exclusion of short wavelengths from the incubation decreased this production (Fig. 4b). The increase in DMSOD

production from this process was accompanied by a decrease in Fv:Fm ratios compared with the initial (i.e., preincubation) values (Fig. 4b). The Fv:Fm ratio of samples incubated in the dark ( $0.46 \pm 0.01$ ) was not significantly different from the Fv:Fm ratio before the start of the incubation ( $0.44 \pm 0.01$ ). Some DMSOd production occurred in the dark because of the particle-associated process, but this amount only accounted for 4% of production from this same process in the full-spectrum light treatment.

DMSOd production from photooxidation was greatest when samples were exposed to the full solar spectrum (Fig. 4b). The change in DMSOd production from DMS photooxidation under the different light treatments was mostly related to wavelength-dependent changes in DMS photooxidation rates (data not shown); the maximum photochemical production of DMSO occurs at approximately 320 nm in the Ross Sea, with production mainly observed between 310 and 350 nm (Westby 2007).

Because of the occurrence of DMS photooxidation in light-incubated samples, DMSOd production from biological DMS oxidation in the different spectral treatments had to be estimated by difference (Eq. 1). This difference was generally small and the propagated error associated with the measure of this process was too large to detect statistically significant differences in DMSOd production from biological oxidation of DMS among spectral treatments. In the dark treatment, biological oxidation of dissolved DMS was the main source of DMSOd, contributing 85% of the total DMSOd production, with the remaining 15% being produced by the particle-associated process.

DMSOd production in seawater collected from different depths: On 14 Nov and 29 Nov 05, seawater was collected from different depths and exposed under the same 32% surface incident irradiance treatment (Fig. 5). Seawater collected on 14 Nov had DMS, DMSOd, DMSPt, and Chl *a* concentrations significantly lower than those of the seawater collected on 29 Nov (Table 2). On both sampling dates, the deepest sample (i.e., 50 m) was taken from below the surface mixed layer, whereas the three shallower samples were taken from within the mixed layer.

Water collected and incubated on 14 Nov showed an increase in DMSOd concentrations of  $0.66\text{--}0.79 \text{ nmol L}^{-1}$ , whereas water collected and incubated on 29 Nov presented an increase of  $7.15\text{--}8.51 \text{ nmol L}^{-1}$  (Fig. 5a,b). Despite the lower UV dose experienced by the samples incubated on 14 Nov compared with those incubated on 29 Nov (Table 3), the DMSOd concentration doubled or tripled during the 14 Nov incubation, whereas it increased only 19–31% from the initial value during the 29 Nov incubation.

The relative importance of the particle-associated DMSOd production process, DMS photooxidation, and biological DMS oxidation, was similar at each depth on a given sampling date (Fig. 5c,d). However, the relative proportions were different between the two sampling dates. On 14 Nov (Fig. 5c), the particle-associated process contributed the most to DMSOd production (71.6–84.5%), whereas on 29 Nov (Fig. 5d), photooxidation was the main source of DMSOd (56.7–83.3%), followed by the

particle-associated process (5.8–38.5%). On both sampling dates, biological DMS oxidation was the minor contributor to DMSOd production (1.0–2.6% and 4.9–11.6%, on 14 Nov and 29 Nov, respectively).

For both sampling dates, DMSOd production from the particle-associated process normalized to Chl *a* concentration was significantly higher in the samples collected from below the mixed layer than in the samples collected from within the mixed layer (Fig. 5e,f).

DMS concentration changes during incubation: The formula employed to calculate both  $\text{DMSO}_{\text{ph}}$  and  $\text{DMSO}_{\text{ph+bo}}$  (Eq. 3) assumes no DMS production during the incubation time. If DMS was produced during incubations in the light,  $\text{DMSO}_{\text{ph}}$  and  $\text{DMSO}_{\text{ph+bo}}$  would be underestimated because the  $^{35}\text{S}$ -DMS tracer would be diluted; therefore, the calculated DMSOd production from the particle-associated process ( $\text{DMSO}_{\text{extra}}$ ) would be overestimated. DMS concentrations could increase because of phytoplankton release (Bauman et al. 1994) and biological conversion of DMSP or DMSO to DMS. We cannot exclude the possibility of some DMS production during the incubations, but our results suggest that any DMS production, and hence dilution of the  $^{35}\text{S}$ -DMS tracer, was insignificant (relative to the size of the DMS pool and the photochemical losses), because there was no difference ( $p = 0.71$ ) between the DMS loss estimated by the tracer approach (see *Methods*) and the net change in DMS concentration as determined by gas chromatography during both light and dark incubations (Fig. 6).

## Discussion

The difference between the net change in DMSOd concentration and the DMSOd produced from the photo- and biological oxidation of dissolved DMS (Figs. 2, 3) provides evidence for at least one other process involved in the production of DMSOd that is clearly stimulated by light, especially UV (Fig. 4b). This unidentified particle-associated process constituted an important source of DMSOd in near-surface waters that was not derived from dissolved DMS. Here, we review the evidence for this process, speculate on its mechanism, and place it in the context of the other DMSO cycling processes in the Ross Sea.

The difference between  $\text{DMSO}_{\text{net}}$  and  $\text{DMSO}_{\text{ph+bo}}$  (Eq. 2) provides the amount of DMSOd produced by processes other than photo- and biological oxidation of dissolved DMS minus any DMSOd loss (e.g., from microbial transformation). Dark DMSOd loss was measured on Nov 05 with  $^{35}\text{S}$ -DMSO, and it was found to be quite low,  $<0.076 \text{ nmol L}^{-1} \text{ d}^{-1}$ , which is insignificant relative to the difference between  $\text{DMSO}_{\text{net}}$  and  $\text{DMSO}_{\text{ph+bo}}$  in most circumstances. Because the dark biological DMSOd loss that we measured was small and DMSO was not photooxidized in Antarctic waters (Toole et al. 2004), we assumed throughout this work that the difference between DMSOd production from  $\text{DMSO}_{\text{net}}$  and  $\text{DMSO}_{\text{ph+bo}}$  was not affected by DMSO losses and that it was equal to the DMSOd production from an unidentified particle-associated process. The assumption of

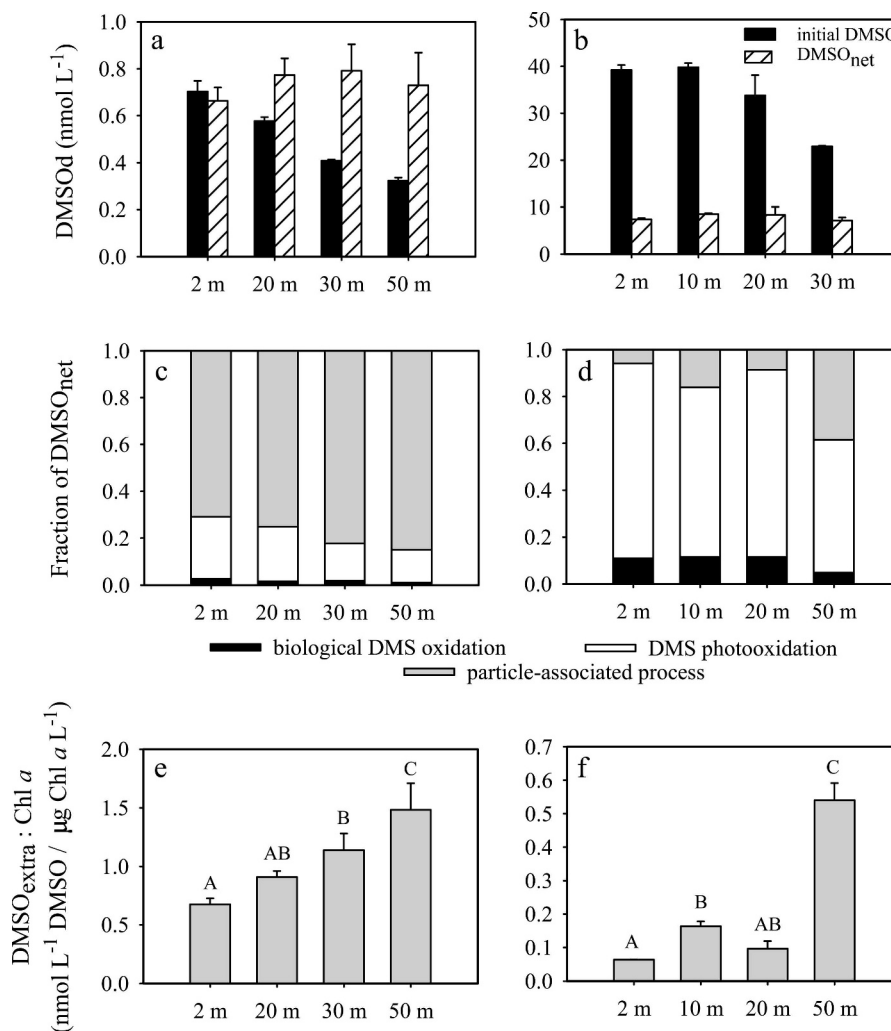


Fig. 5. (a, b) Initial (i.e., preincubation) DMSO<sub>d</sub> concentration for each sampled depth and the amount of DMSO<sub>d</sub> produced (DMSO<sub>net</sub>) during the deck experiment carried out on 14 Nov and 29 Nov, respectively. This experiment consisted of seawater collected from different depths and exposed to 32% attenuated, full-spectrum solar radiation. Note the difference in initial water characteristics (Table 2) and the light dose received (Table 3) for both experiments. (c, d) The fraction of the net DMSO<sub>d</sub> produced during the incubation (DMSO<sub>net</sub>) by biological DMS oxidation (black), DMS photooxidation (white) and the unidentified particle-associated process (gray) on 14 and 29 Nov, respectively. (e, f) DMSO<sub>d</sub> produced by the unidentified particle-associated process (DMSO<sub>extra</sub>) normalized to the Chl *a* concentration for samples collected and incubated on 14 and 29 Nov, respectively. Bars labeled with different capital letters are significantly different (by one-way ANOVA,  $p < 0.05$ ). Error bars denote the calculated standard deviation of the mean. On both days, the sample collected at 50 m was from below the surface mixed layer, whereas the other three samples were collected within the mixed layer.

low contribution of DMSO loss to the overall change in DMSO<sub>d</sub> concentrations is supported by earlier work that found very slow DMSO losses attributable to microbial transformations (Kiene and Gerard 1994). If DMSO losses were larger than we estimated on the basis of whole-water incubations, this would only mean that DMSO<sub>d</sub> production from the particle-associated process was even larger than reported here. Furthermore, because DMS losses measured with the <sup>35</sup>S tracer approach were essentially equivalent to the net losses of DMS measured by GC during the incubations (Fig. 6), it is unlikely that dilution of the added tracer by DMS production in the

light-incubated samples would have affected the calculated DMSO<sub>d</sub> production from the particle-associated process.

Light-induced phytoplanktonic biosynthesis and subsequent release of DMSO is a potential mechanism that would explain the production of DMSO<sub>d</sub> by a particle-associated source, although we do not have direct evidence to support this hypothesis. DMSO has been detected in the particulate pool of seawater and in phytoplankton cultures, and it has been attributed to the production and retention of DMSO within phytoplankton cells (Simó et al. 1998; Simó and Vila-Costa 2006). Lee and de Mora (1996) reported rapid daytime production of DMSO<sub>d</sub> (2.5–

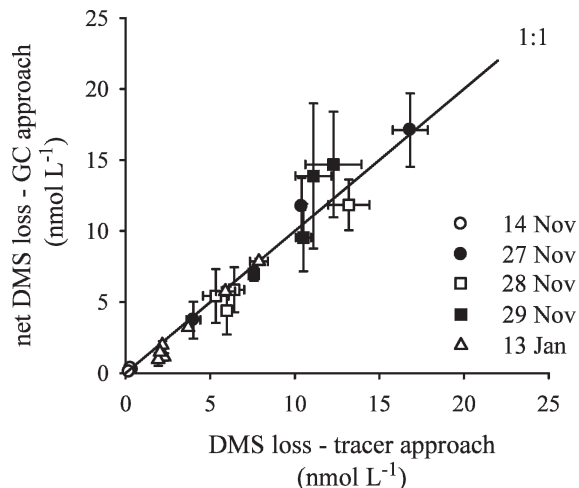


Fig. 6. DMS loss during in situ (28 Nov and 13 Jan) and deck incubations (14, 27, and 29 Nov) calculated from the  $^{35}\text{S}$ -DMS tracer approach compared to the difference between the pre- and postincubation dissolved DMS concentration determined by gas chromatography (GC approach). Data from all light and dark treatments are included for each specific experiment. The line represents the 1:1 relation. Error bars denote the standard deviation of the mean.

$6.0 \text{ nmol L}^{-1} \text{ h}^{-1}$ ) that, according to the authors, was higher than expected from photooxidation and bacterial transformation of DMS, concluding that algal photosynthetic production and subsequent release might have been responsible for the DMSOd increase. Simó et al. (2000) found an increase in DMSOd in dark incubations of seawater and attributed this change to a dark exudation of cellular DMSO. They discounted the biological oxidation of dissolved DMS because the increase in DMSO concentration was not accompanied by a decrease in DMS concentration. However, because they measured net concentration changes of the different sulfur pools, a small production of DMSOd from the biological oxidation of DMS cannot be ruled out. In our deck incubation (Fig. 4b), the particle-associated process was responsible for only 15% of the dark production of DMSOd. Moreover, in the in situ incubation arrays, no dark production was detectable from this process. These results suggest that even though dark production from the particle-associated process cannot be discarded, its importance is probably small compared with dark production of DMSOd from the biological oxidation of dissolved DMS in the Ross Sea.

Considering that DMS, DMSP, and DMSO have been proposed to be part of an antioxidant mechanism for phytoplankton (Sunda et al. 2002), a higher DMSO production in particles from the reaction of cellular DMSP or DMS with reactive oxygen radicals would be expected in samples more prone to suffer oxidative stress. Our results support this hypothesis because DMSO production from the unidentified particle-associated process increased with higher solar light exposure, especially by the UV component of sunlight, and was accompanied by a decrease in the efficiency of photosystem II (Fv:Fm), an index of physiological stress in the phytoplankton (Fig. 4b). More-

over, the DMSOd production:Chl *a* ratios were significantly higher in dark acclimated samples collected from below the mixed layer and exposed to 32% of surface irradiance than in samples collected from the mixed layer (Fig. 5c,d), where presumably the plankton were more acclimated to higher light exposure (Lewis et al. 1984). The idea that non-light-acclimated plankton produce more DMSO in particles once exposed to sunlight is further supported by the observation that particle-associated DMSOd production was a greater fraction of the total DMSOd production in samples collected on 14 Nov compared with 29 Nov, perhaps because of the differences in light history of phytoplankton cells since on 14 Nov, there was still extensive ice cover, whereas on 29 Nov, the Ross Sea polynya was already developed. To determine whether the increase in the dissolved DMSO pool in irradiated samples was accompanied by accumulation of DMSO in particles (i.e., DMSOp), we attempted to measure DMSOp as the difference between total DMSO concentrations (i.e., dissolved plus particulate) and independently determined DMSOd concentrations. The concentration of both total and dissolved DMSO ranged from 0.9 to  $58.0 \text{ nmol L}^{-1}$ , but the difference between the two pools was generally not significant, even though analytical uncertainties for each pool were on the order of 5%, implying that the DMSOp pool was small. When DMSOp concentrations were obtained, statistically significant differences between pre- and postincubation DMSOp concentrations were not detected (data not shown).

Although production of DMSOd from the presence of particles is consistent with its production during oxidative stress inside plankton cells (see above), the pattern of the particle-associated DMSOd production rates that we observed as a function of light exposure was also similar to the pattern of DMSO production from photooxidation of dissolved DMS (Figs. 2, 3). Therefore it is possible that this DMSOd production occurs via photochemical oxidation of DMS or some other sulfur compound in the particle phase. We are not aware of any reports of photoreactive compounds, other than DMS, able to produce DMSO in natural aerobic systems. DMSP, the main precursor of DMS in marine systems, does not photolyze appreciably in the dissolved phase in Antarctic waters (Kieber, unpubl. data); therefore, it is unlikely that photodegradation of DMSP was a direct source of DMSOd in our experiments.

Even though DMSOd production from dissolved DMS photooxidation and the particle-associated process was stimulated by solar radiation, production from biological oxidation of dissolved DMS was negatively affected by it. In the array carried out in Nov 05, inhibition of DMSOd production from DMS oxidation in samples incubated close to the surface (i.e., 2 and 5 m) was apparent from the difference between  $\text{DMSO}_{\text{ph+bo}}$  and  $\text{DMSO}_{\text{ph}}$ , but this difference was not statistically significant. On the other hand, evidence from the Jan 05 in situ array experiment showed that microbial DMS transformation was significantly inhibited by sunlight, with the inhibition increasing toward the sea surface (Kieber et al. 2007). On the basis of results from the in situ incubation arrays, we conclude that biological DMS oxidation is the least important of the

three sources of DMSOd in the top 15 m of the water column (7.6–28.5%). However, quantitative analysis of the array results must be interpreted carefully because of constraints in our experimental design. First, rates were only integrated over the top 15 m. If we extrapolate our results deeper in the water column, then the biological oxidation of DMS to DMSO should become quantitatively more important compared with the light-based processes, and it will be the only process yielding DMSOd below the photic zone (53 and 29 m for Nov and Jan 05, respectively). Second, the in situ array approach we used here is not necessarily representative of the natural system because water from only one depth was incubated at different depths. This is probably not an important issue if the surface mixed layer was relatively homogeneous, as it was in our study. The most important limitation, however, was that the water samples were incubated at fixed depths without mixing, which has been shown to have important and variable effects on phytoplankton photosynthesis (Neale et al. 1998) and bacterial productivity (Huot et al. 2000). By removing mixing, we might have overestimated inhibition of bacterial DMS transformation and therefore underestimated DMSO production via this process in the upper water column. Likewise, given the importance of UV radiation in promoting particulate DMSO production, it is also possible that we overestimated this production term by exposing the samples to higher UV doses than they would experience if mixing were considered.

This work demonstrates that the relative importance of DMSOd production processes is depth dependent, with DMS photooxidation and an unidentified particle-associated process as the main sources of DMSOd close to the surface, where UV light penetrates, and biological DMS oxidation as the main DMSOd production process in the dark. Dissolved DMS is not necessarily the main precursor of DMSOd, especially under high solar light exposure, but the nature of particle-associated DMSOd production requires further investigation.

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