

Dimethylsulfide and major sulfur compounds in a stratified coastal salt pond

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Abstract

We conducted a diurnal study of gradients of dimethylsulfide (DMS), dimethylsulfoniopropionate (DMSP), dimethylsulfoxide (DMSO), and bacterial numbers in a stratified coastal salt pond (Salt Pond, Falmouth, Massachusetts). Microlayer samples were collected with a surface skimmer, a partially submerged rotating glass cylinder that allows the collection of a thin layer of water by adherence to the drum. All sulfur compounds and bacteria increased toward the water surface, with a diurnal signal in DMSP and DMSO. Fractionation of DMSP and DMSO in dissolved (d) and particulate (p) pools revealed that any trend in DMSP was due to the p fraction, and trends in DMSO originated from the d fraction. Photoeffects are important for the distribution of DMSPp and DMSOd. In Salt Pond, the production of DMSP is probably linked to photosynthesis, and photooxidation is of greater importance to the production of DMSO than is biological oxidation.

Dimethylsulfide (DMS) is the major volatile reduced organic sulfur compound in the open ocean and coastal waters: its emission from surface water represents a major flux of biogenic sulfur to the atmosphere (Lovelock et al. 1978) and affects atmospheric chemistry and global climate in various ways (Andreae and Crutzen 1997). DMS is produced by algae but also as a product of microbial decomposition of organic matter. Concentrations of DMS are linked to dimethylsulfoniopropionate (DMSP) and dimethylsulfoxide (DMSO), which are governed by complex biological interactions such as nutrient availability, primary production, senescence of phytoplanktonic DMSP-carriers, zooplankton grazing, and bacterial degradation (Groene et al. 1995). In addition, the DMS-producing communities and chemical processes (e.g., the loss of DMS through photolysis) are affected by physical dynamics of the surface layer (e.g., turbulence) and by meteorological forces such as total solar radiation, ultraviolet (UV) intensity (and spectrum), and wind speed (e.g., Simó and Pedrós-Alió 1999a,b).

In a study of a stratified coastal salt pond reported two decades ago (Wakeham et al. 1984), it was shown that distributions of DMS vary seasonally in response to the changing physical, chemical, and biological characters of the pond's water column. Two processes seemed to be important: the production during algal blooms and the production and/or preservation in low-oxygen conditions. Processes deeper in the water of a stratified column are likely to be of less direct importance to atmospheric chemistry and climate than are surface-water processes. It is widely recognized that processes at the water surface, in the 'microlayer,' determine the concentration disequilibrium with the atmosphere and,

consequently, all transfer (e.g., SOLAS science plan and implementation strategy: www.uea.ac.uk/env/solas/).

The microlayer is a region in which large vertical gradients exist and in which physical, chemical, and biological properties are most altered relative to subsurface water. At the same time, it may be considered as a physical barrier to gas transfer and a microcosm that exhibits physical and chemical properties distinct from the subsurface layers. Studies in the past decade have focused on processes specific to the microlayer of (mainly) the sea surface (e.g., Hardy and Apts 1989; Zhang et al. 1998; Yang and Tsunogai 2005). The importance of photochemical and bacterial conversions of materials in the top layer of the water column is nowadays being increasingly recognized and quantified. Moreover, studies show that such processes may be enhanced in, or may even be specific to, the microlayer (Zemmeling et al. 2005a). Here we present dynamics of DMS and major related sulfur compounds (DMSP and DMSO) in the microlayer of a stratified coastal salt pond.

Materials and methods

Study area—Salt pond is a shallow (5.5-m-deep) eutrophic marine basin on Cape Cod, Massachusetts, which exhibits density stratification (Wakeham et al. 1984). Two diurnal studies were conducted on 8 and 11 September 2003. Wind speed, air, and water temperatures were collected on the pond using a hand-held anemometer (electronic wind-speed indicator, Davis Instruments) and a hand-held thermometer (450 series, Omega), respectively. Solar radiation ($W m^{-2}$) was measured using an Eppley Model PSP (Precision Spectral Pyranometer) deployed from the marine shore laboratory, situated on Martha's Vineyard, Cape Cod, Massachusetts. The presented meteorological data are averages over the duration of the sampling period plus 5 h prior to the sampling period.

Microlayer sampling—The sea surface was sampled every 6 h (from noon forward) with a surface microlayer skimmer, as described by Zemmeling et al. (2005b). Briefly, the skimmer consists of a rotating glass cylinder (15 cm in diameter) that is partially submerged to 5 cm in depth (Frew

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et al. 2002). The cylinder rotates at a speed of 23 rotations min^{-1} while collecting a thin layer of water (uppermost 50 μm of the water column) by viscous retention. Adhering water is wiped off the cylinder and collected in a 100-mL vial in about 1.5 s. The water is subsequently transferred at an 80 mL min^{-1} flow (using peristaltic pumps) to a 4.4-liter dark glass bottle. A second sampling line was mounted near the skimmer and supplied subsurface water from 10 cm in depth (at 80 mL min^{-1} flow). The drum and second sampling line are supported by a small catamaran that is attached by a 2-m-long beam to a Boston Whaler. This set-up allows the skimmer to respond to sudden changes in surface roughness as it easily follows wave sizes up to 0.5 m. In this manner the catamaran is pulled alongside the boat at a speed of 1 m s^{-1} , using the electrical propulsion of the boat. Samples from 200 cm in depth were collected with Niskin bottles and immediately transferred to darkened glass bottles.

Typically, 4.4-liter samples of all depths were collected over a 60-min period and were returned to the laboratory for immediate analysis (of DMS), or were treated for overnight hydrolysis and next-day analysis (DMSP), or were reduced and stored for later analysis (DMSO) within 72 h.

Analysis of DMS and major sulfur compounds—DMS was stripped from 4-mL subsamples by vigorous bubbling with N_2 at about 120 mL min^{-1} for 6 min. Subsequently, the compounds were trapped in Carboxen 101 held at room temperature in 0.64 cm (outer diameter) glass-lined Sulfinert (Restek Corporation) tubing. DMS was desorbed into a gas chromatograph (GC) by heating to approximately 180°C and was analyzed by a Sievers chemiluminescence detector (detection limit 5×10^{-13} mol) after separation on Chromosorb 330 (Supelco). Unfiltered and gravity-filtered (Whatman GF/F) water was used for the analysis of DMS. There was no significant difference between DMS concentrations from filtered and unfiltered water samples ($n = 14$, $p < 0.05$), and the average of both treatments was used for further analysis.

Filtrate was divided into three 50-mL glass reaction vials for subsequent analysis of dissolved fractions of DMSP (DMSPd) and DMSO (DMSOd), taking two subsamples from each vial; results are presented as averages ($n = 6$) with one standard deviation from the mean. NaOH was added to each DMSP sample to bring the OH^- concentration to 1 N; this catalyzes the conversion of DMSP to acrylic acid and DMS. Samples were capped with Teflon-lined serum stoppers after addition of OH^- and stored at 4°C until analysis.

Our procedure for DMSO analysis follows in general that of Kiene and Gerard (1994); we used titanium trichloride (TiCl_3) for the reduction of DMSO to DMS. The following changes were made to the Kiene and Gerard protocol; TiCl_3 (stabilized solution, Fisher Scientific) was heated to 50°C and bubbled with N_2 for 2 h, and all glassware was muffled overnight at 400°C and rinsed with sparged TiCl_3 prior to usage. TiCl_3 was cooled to room temperature before 10 mL was added to a 40-mL seawater sample. The reaction vial was immediately closed and kept at 4°C until analysis. Prior to analysis of the produced DMS, reaction vials were placed in a water bath at 50°C for 2 h to ensure full conversion of DMSO to DMS. After the heating step, the vials were al-

lowed to cool to room temperature. A glass syringe (rinsed with TiCl_3) was used to pull subsamples of 4 mL through the septum that sealed the reaction vial and to inject the sample into the sparger that remained sealed with a septum.

Particulate DMSP (DMSPp) and DMSO (DMSOp) were determined from triplicate 50-mL vials of unfiltered water ($n = 6$) and subsequent subtraction of the amount for respective concentrations found in filtrates and concentrations of DMS. All samples and standards were analyzed in triplicate with an analytical precision of 10% at the 10 nmol L^{-1} range. DMS generated from base digestion of DMSP and reduction of DMSO was measured following the procedure described for DMS. However, one adaptation was made to analyze DMSO samples; after bubbling to strip DMS from the treated seawater, the gas passed a trap containing solid Na_2CO_3 in order to neutralize acids before concentration onto Carboxen X and subsequent desorption into the gas chromatograph.

The GC was calibrated with standards prepared by injecting a sample of DMS from a calibrated permeation tube. Standards for DMS (Sigma Aldrich) were prepared in methanol. DMSO standards were made in 20% TiCl_3 (diluted with Milli Q water). The diluted TiCl_3 was heated to 50°C and bubbled with N_2 for 2 h prior to use to prevent contamination with DMSO; this step, together with extensive muffling and rinsing of glassware before usage, gave an offset in blanks of about 0.5 nmol L^{-1} . Subsequently, the TiCl_3 solution and 99.9% DMSO (Fisher Scientific) were cooled to 4°C before dilution into a working stock. Reaction vials were immediately sealed with a Teflon septum and stored at 4°C until usage (within a week after preparation). Cooling to 4°C slowed the reduction of DMSO; it took over 72 h before 60% of the total DMSO was reduced. Prior to analysis the standards were heated to 50°C for 2 h. Comparison of standards that were directly analyzed after addition of TiCl_3 and standards that were stored for a week after addition did not reveal a significant difference between either treatment ($n = 12$, $p < 0.05$).

Bacterial numbers—Subsamples of 4.5 mL were taken from the 4.4-liter seawater samples and immediately fixed by 1% (final concentration) formaldehyde and stored at 4°C in the dark until analyses (within 24 h). For bacterial counts, a volume of 1 mL was incubated for 5 min with 4 μL Acridine Orange (final concentration, 0.01%) and subsequently filtered onto black 0.2- μm Nuclepore filters (Hobbie et al. 1977). After staining, cell numbers were immediately counted on a Zeiss epifluorescence microscope.

Results and discussion

Meteorology—Conditions during the sampling periods varied slightly (Fig. 1). Wind speed (U) ranged from 1.3 to 3.6 m s^{-1} (Fig. 1a), resulting in a smooth water surface with an estimated wave size of less than 5 cm. Air temperatures (Fig. 1b) varied from 14°C to 21°C, with maxima during the day, while water temperatures remained constant around 16.3°C. Irradiation (Fig. 1c) during the two sampling days varied from -3 W m^{-2} at night to 580 W m^{-2} during day-

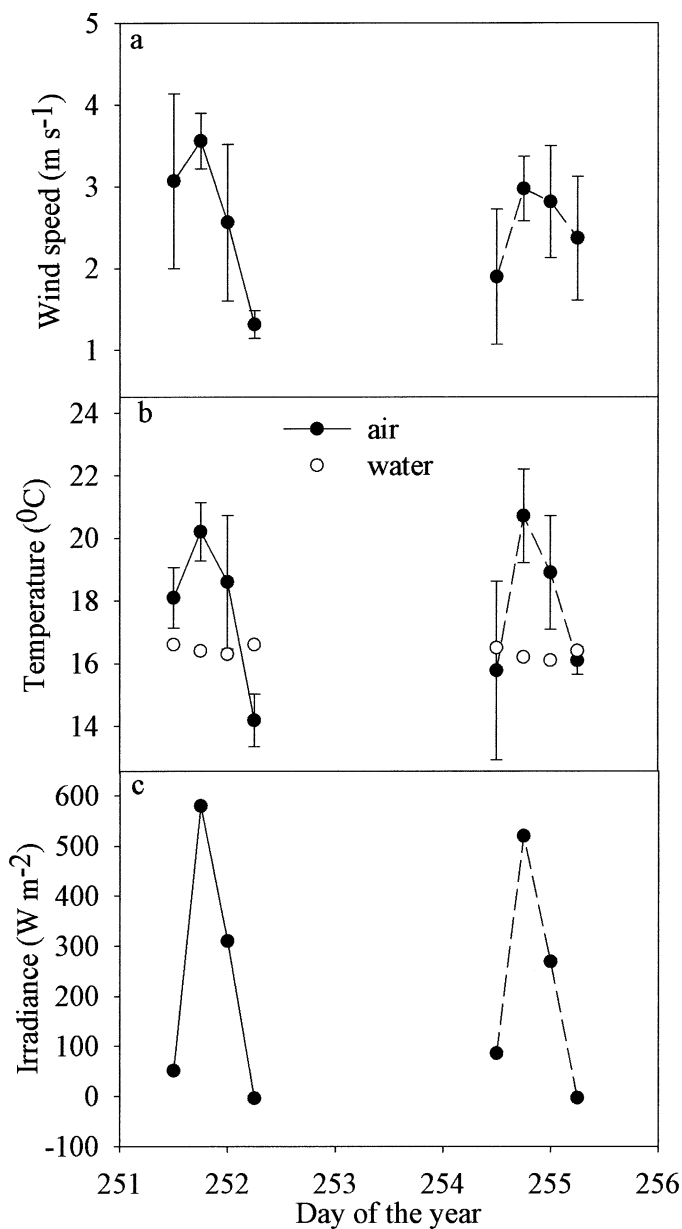


Fig. 1. Meteorology at day of the year (GMT) 251.5–252.25 and 254.5–255.25. Data are average meteorological conditions met at Salt Pond 5 h prior to the sampling period and during the sampling period; error bars represent maxima and minima. (a) Wind speed (m s^{-1}), (b) air temperature and water temperature ($^{\circ}\text{C}$), and (c) solar radiation (W m^{-2}).

time (based on 6-h averages), with only a minor difference between maxima of both days.

DMS concentrations increased from 4 nmol L^{-1} at 2 m in depth to $8\text{--}9 \text{ nmol L}^{-1}$ at the water surface, with no apparent diurnal trend at any depth (Fig. 2). With atmospheric values that are typically three orders of magnitude lower, the net exchange direction is from the water surface to the air. In the two-layer approach of air–sea exchange (Liss and Slater 1974), the oceanic flux of a gas is the product of the total gas transport velocity K_T and the partial pressure difference across the air–sea interface,

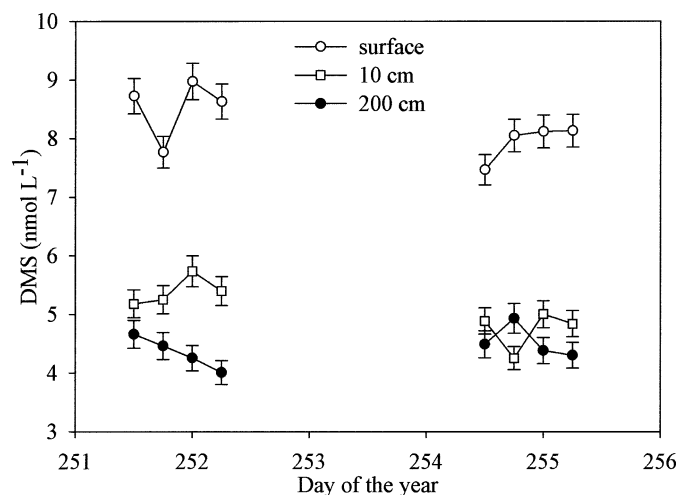


Fig. 2. DMS concentrations (nmol L^{-1}) in the microlayer, at 10 cm in depth, and at 200 cm in depth at day of the year 251.5–252.25 and 254.5–255.25. Error bars are one standard deviation from the mean ($n = 6$).

$$F = K_T(C_w - C_g/H) \\ = (1/\alpha k_w + 1/Hk_g)^{-1}(C_w - C_g/H) \quad (1)$$

where C_g is the atmospheric boundary layer concentration above the gas-phase film, C_w is the water concentration below the aqueous-phase film, H is the dimensionless Henry's law constant for DMS (Dacey et al. 1984), k_w and k_g are exchange constants for liquid and gas phases, and α is a chemical enhancement factor due to reactions in the sea-surface microlayer (assumed to be 1 for DMS; Liss and Slater 1974). For sparingly soluble gases, the total gas-exchange coefficient can be approximated to the liquid-phase gas-exchange constant k_w , calculated using semiempirical formulations involving wind speed and the temperature-dependent Schmidt number of the gas (Liss and Merlivat 1986; Wanninkhof 1992; Nightingale et al. 2000). The gas-exchange constant over Salt Pond can be estimated according to the Liss and Merlivat (1986) parameterization of gas transfer over smooth surfaces for wind speeds (U) up to 3.6 m s^{-1} (other parameterizations are based on wind speed data over 3.6 m s^{-1}),

$$k_w = 0.17U(\text{Sc}/660)^{-2/3} \quad (2)$$

where the Schmidt number (Sc) for DMS is calculated from Saltzman et al. (1993) and is normalized to 660, the Schmidt number of CO_2 in sea water at 20°C . Surface-water concentrations of around 9 nmol L^{-1} would result in fluxes of 635 to $953 \text{ nmol m}^2 \text{ d}^{-1}$, while fluxes derived from water samples from 10 cm in depth would only be half of this amount. Thus, the residence time in the microlayer ($\sim 50 \mu\text{m}$) via air–sea exchange is $40\text{--}60 \text{ s}$ at the wind speeds encountered. However, gas exchange does not only depend on wind speed and temperature but also on other environmental parameters, such as surface films, subsurface turbulence, and waves. These factors are intermittently linked and influence gas exchange either directly or indirectly. Zemmeling et al. (2005b) found a stronger relationship between DMS gradients toward

the sea surface and wave height than between gradients and wind speed. In Salt Pond, a limited fetch over the lake might avoid the build-up of larger waves, and stratification toward the water surface can be expected. In addition, biological degradation products other than sulfur compounds might accumulate more toward the surface of the water column of an enclosed pond than toward the surface of the open ocean, which could cause an increase of viscosity that suppresses wave formation. (It has to be emphasized that the microlayer is not a discrete layer lying on the surface, as a slick does.) The stability in the water column will result in low gas-exchange rates and thus enhanced residence times.

Zemmelink et al. (2005b) tested the suitability of the skimmer for the sampling of volatile compounds in the microlayer. It was concluded that loss of volatile compounds from the skimmer to the atmosphere is unavoidable and that surface DMS values are significantly underestimated by the use of this technique. This loss can be estimated by using the above mentioned gas-exchange parameterizations. Note that the wind speed over the drum is influenced by the rotation speed and the propulsion velocity of the catamaran. The wind speed (which can be seen as an air renewal rate) around the drum has, therefore, an offset of about 1.2 m s^{-1} . Based on Eqs. 1 and 2, the residence time of DMS at this air renewal rate is about 2 min. At ambient wind speeds of 4 m s^{-1} , the air renewal rate around the skimmer could increase to 5.2 m s^{-1} . The water surface would be in the regime of so-called rough conditions (Liss and Merlivat 1986), during which gas-exchange constants can be calculated by using

$$k_w = 2.85U - 9.65(\text{Sc}/660)^{-1/2} \quad (3)$$

for wind speeds between $3.6 \text{ m s}^{-1} < U \leq 13 \text{ m s}^{-1}$. This enhanced wind speed of 5.2 m s^{-1} decreased the residence time of DMS on the skimmer to 5 s.

The residence time of DMS on the skimmer appears to be longer than 1.5 s in wind speeds up to 8.8 m s^{-1} . This is an important realization, because 1.5 s is the time that it takes to wipe the adhered water off the drum and to collect it into a vial. It is therefore tempting to conclude that the gradients toward the microlayer of Salt Pond are real. However, during laboratory studies, using a well-mixed water column, Zemmelink et al. (2005b) observed that degassing on the skimmer resulted in a 70% loss of DMS at wind speeds of 3 m s^{-1} . Even at a wind speed of 0 m s^{-1} (renewal rate of 0.18 m s^{-1} , due to the rotation speed), measured losses were about 50%. An explanation of this loss factor could come from the possible enhancement of turbulence in water that is adhered to the drum, compared to turbulence in the water column. The turbulence on the drum can be generated in several ways: by the mixing rate of the water in the tank (400 L h^{-1}), wind blowing and pushing water against the drum, resonance in the drum, and by water that is pushed up against the wiper by the rotation of the drum. The loss on the drum during laboratory tests indicates that the skimmer introduces a significant sampling artifact that cannot readily be accounted for. This observation also indicates that the observed gradient toward the water surface of Salt Pond, and therefore fluxes to the atmosphere (but also to deeper water), are significantly underestimated when based on samples that are

collected by a skimmer. However, in our opinion, the skimmer has significant advantages over other techniques that are nowadays used to sample the sea surface. One of the more popular approaches is to pull a film of water from the surface by adherence to a screen or plate (Zhang et al. 1998, 2003; Yang 1999; Yang et al. 2001). The problems related to this technique are extensively discussed in Yang et al. (2001), Yang and Tsunogai (2005), and Zemmelink et al. (2005b). Briefly, manually submerging and withdrawing a grid to a constant depth and at a constant speed is very difficult from a moving platform (while the skimmer rides the waves and skims the water surface at constant speed and depth); the handling time of plates (withdrawal from the surface and pouring sample into collection vessels) is long and difficult to control, which inevitably will lead to substantial loss of volatile compounds and probably also of other substances (the adhered water on the skimmer is easily whipped off and collected in less than 2 s); moreover, it is likely that a residue remains on a grid, the skimmer allows the continuous collection of water over a large surface area.

DMSP concentrations at the water surface are about 4 nmol L^{-1} higher than values at 10 and 200 cm throughout the measurement period ($n = 6$, $p < 0.05$; Fig. 3a). In addition, a small increase of total DMSP was found during the daytime at the 11th (Fig. 3a). Distinguishing between particulate and dissolved DMSP pools (DMSPp and DMSPd, respectively) reveals that DMSPp concentrations increase toward the surface and that they tend to increase during daytime (Fig. 3b). This trend is not very strong and is only significant at the water surface at the 11th ($n = 6$, $p < 0.05$). In contrast, the dissolved fraction does not show any gradient toward the water surface, nor does it show a diurnal signal (Fig. 3c). Hence, any trend observed in total DMSP is due to the particulate fraction. This is in agreement with a recent finding by Simó et al. (2002), who concluded that the rate of DMSP synthesis is linked to photosynthesis, showing a diurnal signal of particulate DMSP. Concurrently, Sunda et al. (2002) proposed that DMSP and its breakdown products (including DMS and DMSO) function as part of a high-capacity cellular antioxidant system that readily scavenges hydroxyl radicals and other reactive oxygen species. Photoeffects are likely to become important for the DMS pool when stratification traps some part of the plankton community near the surface. This could enhance accumulation of DMSP in algal cells and could also result in extra lysis of DMSP to DMS. Both processes would result in the increase of DMS and DMSP toward the surface, as was observed in this study. In addition, it was recently shown that diurnal vertical migration of dinoflagellates can generate diurnal variations in particulate DMSP concentrations in the water column (Belviso et al. 2000; Merzouk et al. 2004). Whether diel variations at the microlayer and at 10 cm are linked to migration of dinoflagellates or other changes in the plankton community has, however, not been studied in Salt Pond.

DMSP is considered to be the key link between algal cells and atmospheric DMS. However, linking phytoplankton to DMS through DMSP is not straightforward. Attempts to correlate DMS to phytoplankton biomass or primary production have failed in most cases (Kettle et al. 1999). This might

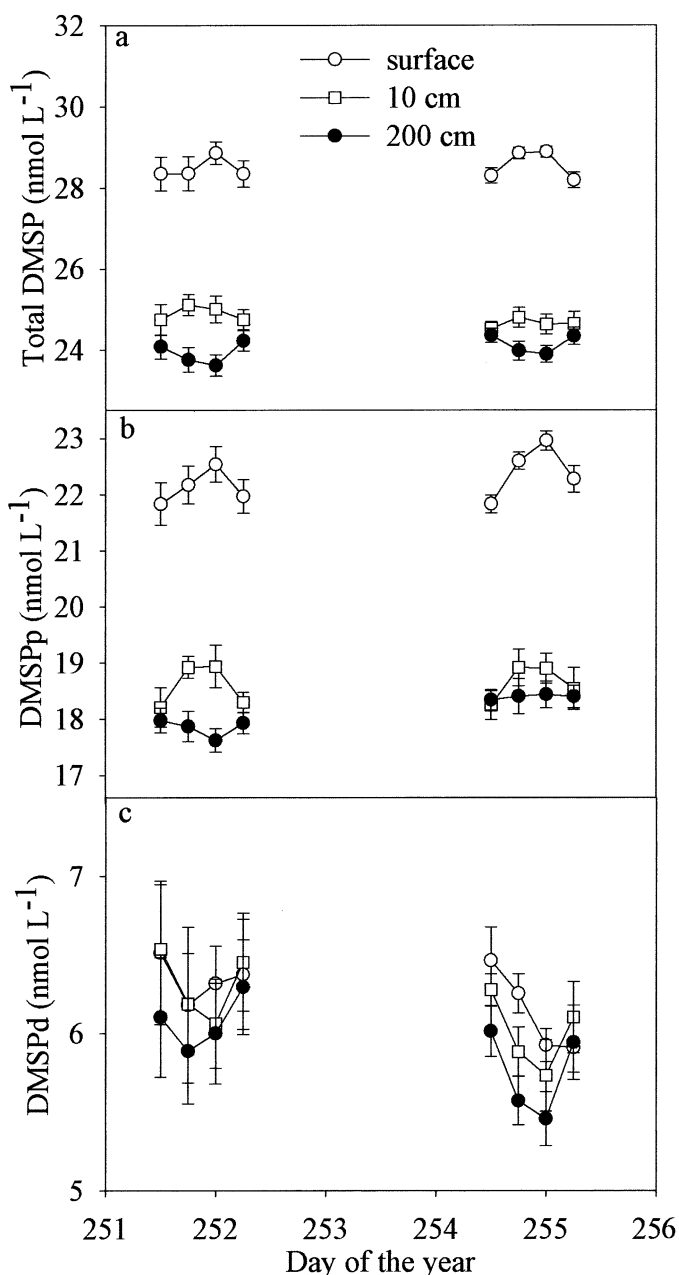


Fig. 3. DMSP concentrations (nmol L⁻¹) in the microlayer, at 10 cm in depth, and at 200 cm in depth at day of the year 251.5–252.25 and 254.5–255.25. Error bars are one standard deviation from the mean ($n = 6$). (a) Total DMSP concentrations, (b) particulate DMSP concentrations, and (c) dissolved DMSP concentrations.

not only be caused by the taxonomy dependence of DMSP production in algae, but also because most breakdown of DMSP into DMS requires that DMSP is released into the water. Fractionation of the DMSP pool into particulate and dissolved phases shows that both can behave completely differently in the water column, which is relevant to the distribution of DMS. It could be that the absence of a gradient of the dissolved DMSP fraction (Fig. 3c) and the strong DMS gradient (Fig. 2) in Salt Pond are the result of a very

effective conversion of dissolved DMSP to DMS toward the surface. Simó and Pedros-Alió (1999a) showed that the efficiency of the DMSP-to-DMS conversion increases as the depth of the mixed layer decreases, to an extent that more than 50% of the DMSP can be transformed into DMS. Such conversion includes, however, intracellular DMSP cleavage in algae and its release as DMS. A large fraction of DMSP is utilized through pathways that do not produce DMS (Kiene et al. 1999; Kiene and Linn 2000). The absence of a gradient of DMSP toward the surface might be linked to an enhanced DMSP utilization by bacteria that show an increase in numbers toward the water surface (see below). However, there is evidence that UV reduces microbial DMSP utilization (Slezak et al. 2001), an effect that would be most pronounced at the water surface. UV exposure can reduce DMS utilization as well. Overall, an increased DMS release by stressed algae together with a decreased DMS consumption by inhibited bacteria (both features caused by high UV-B exposure) might well explain the accumulation of DMS in the microlayer.

Although marine DMS is almost exclusively derived from the degradation of DMSP, it is possible that DMS is formed by a process less linked to DMSP. Production from microbial decomposition of organic matter has been reported and might be another source of DMS in coastal areas.

Total DMSO concentrations in Salt Pond varied from 18 nmol L⁻¹ at 200 cm in depth to 23 nmol L⁻¹ at the water surface, with a significant difference between depths ($n = 6$, $p < 0.05$). This indicates that most DMSO is formed and trapped at the water surface. More interesting is the occurrence of a clear diurnal signal with a sharp increase of surface values by about 1 nmol L⁻¹ at the 8th and the 11th, respectively. A similar increase was also observed at 10 cm in depth but not at 200 cm in depth (Fig. 4a). The gradients and diurnal signals in DMSO are not significant in the particulate pool ($n = 6$, $p < 0.05$; Fig. 4b), although results do indicate a small increase of this fraction toward the water surface. Gradients are significant in the dissolved fraction ($n = 6$, $p < 0.05$; Fig. 4c). An enhanced conversion of DMS to dissolved DMSO in the surface of a stratified water column can be expected as a result of photooxidation and would lead to the observed gradients (Fig. 4c).

Although significant progress has been made in elucidating the processes involved in the production and transformation of DMSO (Hatton et al. 2004), DMSO biochemistry is less well understood than the biochemical cycles of DMS and DMSP. It is generally accepted that DMS oxidation, either photochemically or by phototrophic bacteria, could lead to DMSO formation (Brimblecombe and Shooter 1986). Photolysis is an important removal process for DMS (Kieber et al. 1996; Hatton 2002; Toole et al. 2003) and occurs predominantly between wavelengths of 380 and 460 nm; however, results obtained by Hatton (2002) indicate that UV-B radiation (with wavelengths between 280 and 315 nm) may play an important role in removal of DMS from surface waters. Although it has been determined that photolysis rates are highest close to the surface and sharply decline with depth, the above-mentioned studies demonstrate that photooxidation of DMS is not confined to the upper water column. Results found in Salt Pond confirm that DMSO formation

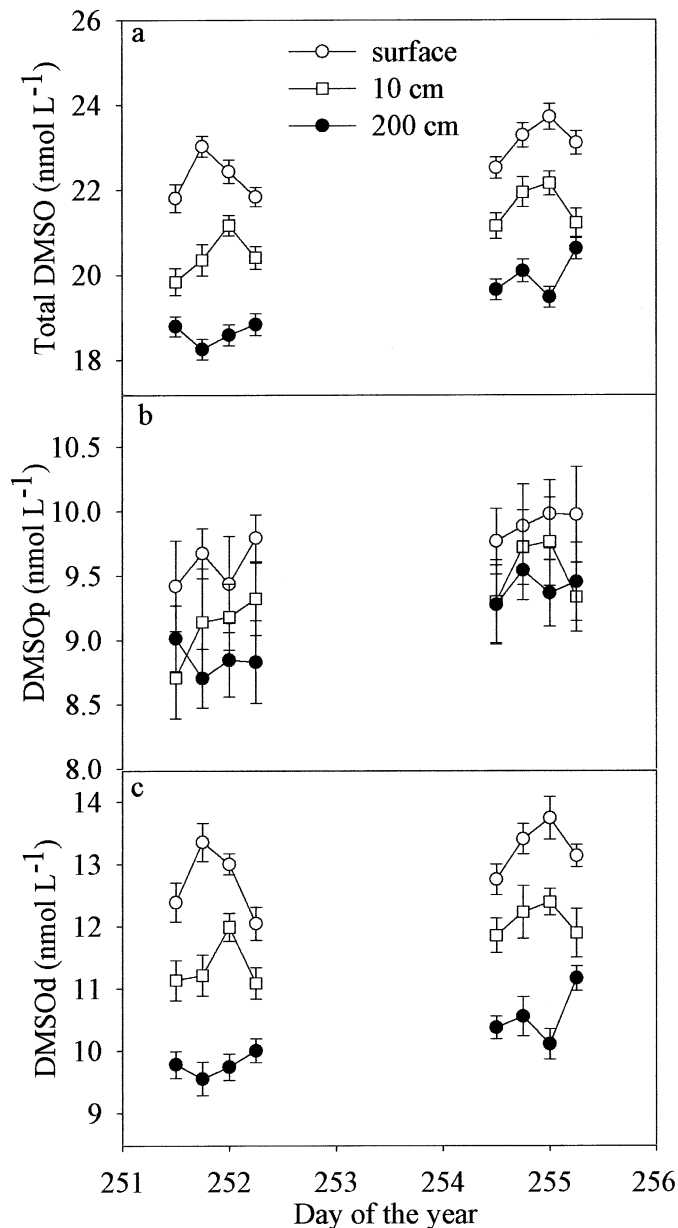


Fig. 4. DMSP concentrations (nmol L⁻¹) in the microlayer, at 10 cm in depth, and at 200 cm in depth at day of the year 251.5–252.25 and 254.5–255.25. Error bars are one standard deviation from the mean ($n = 6$). (a) Total DMSO concentrations, (b) particulate DMSO concentrations, and (c) dissolved DMSO concentrations.

occurs throughout the water column and, moreover, that it is enhanced toward the water surface during daytime (Fig. 4c).

DMS photooxidation appears to depend on photosensitizers present in seawater that are part of the colored dissolved organic matter (CDOM) pool (Tool et al. 2004). CDOM originates from primary productivity and food web processes and is the main factor that controls the penetration of UV irradiance in the water column (Mopper and Kieber 2000). This results in a complex interaction between irradiation, the

food web, and sulfur and carbon cycles, which might result in distinct biochemical differences between water layers of a stratified pond. Unfortunately, the current study does not provide insight into the distribution of CDOM and activity of microorganisms in the water column.

There is increasing circumstantial evidence of a direct biosynthetic pathway of DMSO. Particulate DMSO has been measured in various environments (e.g., Bouillon et al. 2002; Besiktepe et al. 2004); organisms could benefit from intracellular DMSO, as it is known to be a cryoprotectant and an efficient scavenger of free radicals; it has been suggested that it may offer a protection against reactive oxygen radicals generated during photosynthesis (Lee and de Mora 1999). However, distinguishing between the particulate and dissolved pools of DMSO in Salt Pond (DMSOp and DMSOd, respectively) does not indicate a diurnal signal of the particulate fraction (Fig. 4b) but rather an increase of DMSOd during both mornings (Fig. 4c). The results indicate that the particulate pool, which is smaller than the dissolved pool, does not respond quickly to changes in irradiation. However, since DMSO is produced by DMS oxidation but at the same time is consumed by oxidation into methane sulfinic acid (Sunda et al. 2002), it is not clear whether an enhancement of active radical scavenging should result in an increase or decrease of intracellular DMSO.

Surprisingly, surface DMSO concentrations decrease during the night, a pattern that seems to be accompanied by a small increase of DMSO at 200 cm in depth (Fig. 4a). This change is only observed in the dissolved fraction; the distribution of the particulate fraction remains constant. It is difficult to make any statement about the cause without any further measurements, but the decrease observed at the surface might be an effect of dilution of the surface layer with deeper water after cooling during the night (when the air temperature drops below the water temperature; Fig. 1) destabilizes stratification and thus enhances mixing.

In addition to photooxidation of DMS in the water column, DMSO can be produced via transformation from the intracellular to the dissolved phase. This presumably occurs via leakage from healthy cells but mainly via grazing and cell senescence (as with dissolved DMSP). The absence of any daytime trend in the DMSOp results of Salt Pond indicates that an enhanced release of DMSOp into the DMSOd pool during the day does not occur. It seems unlikely that the very weak gradients of DMSOp are a result of enhanced lyses of algae in deeper water because of the absence in gradients of DMSPd. The absence of a significant stratification of particulate DMSO and dissolved DMSP indicates that for the production of dissolved DMSO, photooxidation of DMS is of greater importance than biological oxidation in Salt Pond.

When released into the water, DMSO may be metabolized by bacteria (Taylor and Kiene 1989). In the marine environment, possible bacterial consumption of DMSO has only been observed during dark incubations with natural seawater (Simó et al. 2000). In addition, an extra sink for DMSO might be oxidation to dimethylsulfone (Taylor and Kiene 1989; Lee and de Mora 1996), a reaction that is likely to form a favorable source of energy (Lee and de Mora 1999). The observed decrease in DMSOd might (in addition to a

change in turbulence characteristics) be a result of ongoing nighttime metabolism and oxidation of the dissolved fraction by bacteria, while photooxidation of DMS comes to a halt.

However, it is possible that the presented values of dissolved and particulate fractions of DMSP and DMSO are erroneous, because some species of phytoplankton, and possibly microzooplankton, are known to burst when exposed to (and dried in) air (Goldman and Dennet 1985). Although collection of Salt Pond samples into vials occurs within 2 s and although algae are always submerged in water, susceptibility of some marine phytoplankton species to cell breakage during sampling on a thin-film sampler might occur but would be accompanied by an increase in all dissolved fractions. The fact that this is not observed for DMSPd implies that this artifact is negligible during this study. In addition, elevated daytime values of DMSP and DMSO in the microlayer might be an effect of increased oxidative stress and photooxidation on the surface of the collection drum. However, results indicate that diurnal trends also appear in water collected at 10 cm in depth, indicating that the observed diurnal trends are not solely due to this second effect. In addition, one could argue that processes observed in the water adhered to the drum are equal to processes in a stable microlayer at the water surface. Hence, the gradients observed during this study are real, but the observed diurnal signal might be affected, at least to some extent, by the sampling technique.

Marine bacteria play a role in the transformation of DMS via consumption (Kiene 1992) and of DMSP via DMS and non-DMS-producing degradation (González et al. 1999, 2000; Kiene and Linn 2000) and possibly in the turnover of DMSO. Kieber et al. (1996) compared the photochemical DMS removal to biological removal and loss via atmospheric ventilation in different layers of the euphotic zone. In most cases, biological removal exceeded the photochemical removal in the 0–1-m and 0–20-m surface layers. Because bacteria exert a controlling role on DMS concentration, it is important to improve our understanding of their role in the DMS cycle.

Bacterial numbers in Salt Pond varied from 13.7×10^6 to 15.5×10^6 cells mL^{-1} (Fig. 5), with higher values found toward the water surface, although differences between the surface and 10-cm depth are not always significant. The difference between the surface and 200-cm depth indicates, however, that there is at least some bacterial stratification in the water column. The distribution of bacterial numbers through the water column does not, however, provide insight into the possible existence of a specific depth distribution of bacteria that is closely linked to the sulfur cycle. *Roseobacter*, for example, is known to be involved in degradation of DMSP and for its abundance in coastal waters (González et al. 2000) and might show a preference for high concentrations of DMSP and therefore be more abundant toward the water surface. A more-detailed study of the microbial (and plankton) population and its specific activity (linked to its composition but also to environmental forcing factors such as DOM and UV) would be very interesting but was, however, not within the scope of this study.

It is now widely recognized that interactions between oceans and atmosphere play a major role in climate, via ex-

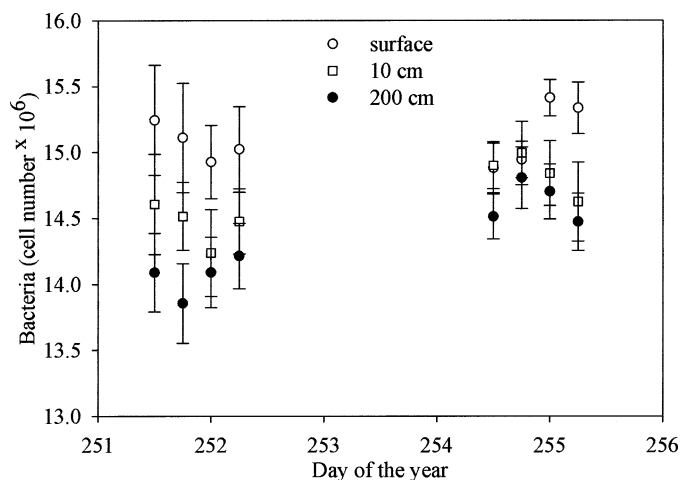


Fig. 5. Bacterial cell numbers (10^6) in the microlayer, at 10 cm in depth, and at 200 cm in depth at day of the year 251.5–252.25 and 254.5–255.25. Error bars are one standard deviation from the mean ($n = 6$).

changes of heat, trace gases, and particulate materials. At the interface between air and water is the surface microlayer, through which all transfers occur. The microlayer is a dynamic layer that is part of the underlying water column (in contrast to a slick), where large vertical gradients exist and where physical, chemical, and biological properties are most altered relative to subsurface water. Hence, its absolute depth is not straightforward to define.

The sea-surface microlayer is found to contain elevated levels of nutrients, bacteria, and sulfur compounds compared to underlying bulk water (Kjelleberg et al. 1979; Plusquellec et al. 1991; Yang 1999; Yang et al. 2001). Changing biological and chemical characteristics of the water column with depth are also apparent in Salt Pond: a persistent stratification of particulate matter, including bacteria, and the increase in concentrations of major sulfur compounds (DMS, DMSP, DMSO) toward the water surface.

Photoeffects seem to be of importance to the distribution of DMSP and DMSO. Gradients in DMSP are solely due to gradients in the particulate fraction, of which the production might be linked to photosynthesis, as concentrations of DMSPp also show a diurnal trend. The dissolved DMSP pool is homogeneously distributed throughout the surface water column with no apparent diurnal signal.

The stratification and diurnal signals found in the total pool of DMSO are primarily due to the distribution of the dissolved DMSO fraction that most likely originates from the photooxidation of DMS.

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