JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 101, NO. C2, PAGES 3715–3722, FEBRUARY 15, 1996

Impact of dimethylsulfide photochemistry on methyl sulfur cycling in the equatorial Pacific Ocean

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Abstract. Shipboard experiments were conducted in the equatorial Pacific Ocean to ascertain the relative importance of atmospheric ventilation, biological consumption, and photolysis in the removal of dimethylsulfide (DMS) from seawater. Comparisons were made at a series of sampling locations in a transect from 12°N 140°W to 12°S 135°W, as part of the International Global Atmospheric Chemistry project's Marine Aerosol and Gas Exchange cruise in February–March 1992. Turnover rate constants for DMS were used to compare the different removal pathways over three depth intervals (0–1 m, 0–20 m, and 0–60 m). In the surface mixed layer (0–60 m) the DMS turnover rate constants ranged from 0.02 to 0.19 day^{-1} for atmospheric ventilation, 0.04 to 0.66 day^{-1} for biological consumption, and 0.05 to 0.15 day^{-1} for photolysis. When all three processes are considered, the corresponding turnover time for DMS ranges from 1 to 4 days, with photolysis accounting for 7%–40% of the total turnover of DMS. Laboratory irradiations were conducted with stored seawater samples to study the kinetics and wavelength dependence of DMS photolysis. Salient results were (1) the photolysis of DMS followed pseudo first-order kinetics, (2) dimethylsulfoxide was a minor (14%) product of DMS photolysis, and (3) the photolysis of DMS in seawater under natural light conditions occurred primarily at wavelengths between 380 and 460 nm. On the basis of these results, we predict that the photolysis of DMS will occur at appreciable depths in the photic zone in oligotrophic marine environments (~60 m). An important finding of this study is that atmospheric loss, biological consumption, and photolysis are all important removal pathways for DMS in the photic zone of the equatorial Pacific Ocean. The relative importance of each pathway is a function of the depth interval considered, sampling location, and meteorological conditions.

Introduction

The biogenic production of dimethylsulfide (DMS) in seawater and its subsequent release to the troposphere is the principal source of organic sulfur to the remote marine atmosphere [*Barnard et al.*, 1982; *Andreae and Raemdonck*, 1983; *Bates et al.*, 1992]. This oceanic efflux is significant because DMS is an important precursor of aerosols and cloud condensation nuclei and thus affects the Earth's radiation balance and climate [*Bonsang et al.*, 1980; *Bigg et al.*, 1984; *Charlson et al.*, 1987; *Prospero et al.*, 1991; *Ayers and Gras*, 1991; *Berresheim et al.*, 1993]. Oceanic DMS emissions are partly a function of surface concentrations of DMS in seawater, which, in turn, are regulated by imbalances in the rates of biological, physical, and chemical sources and removal processes for DMS in the water column. Currently, we have a poor understanding of the dynamics of these processes in seawater.

The primary source of DMS in seawater is through the enzymatic decomposition of dimethylsulfoniopropionate (DMSP), which is derived from algae in the photic zone [*Burgermeister et al.*, 1990, and references therein]; abiotic decomposition of DMSP is negligible [*Dacey and Blough*, 1987]. Culture studies support the supposition of a biological source of DMS in seawater [*Vairavamurthy et al.*, 1985; *Dickson and Kirst*, 1986, 1987a, b; *Keller et al.*, 1989], but often DMS concentrations are poorly correlated with algal parameters (e.g., chlorophyll *a* and primary productivity). This general lack of covariance suggests that specific algal species produce DMS (see *Malin et al.* [1992] for review) and/or that other processes, such as zooplankton grazing [*Dacey and Wakeham*, 1986], are periodically important.

There is considerable uncertainty regarding the removal of DMS from seawater. Historically, the primary removal of DMS from the surface mixed layer was attributed to its atmospheric ventilation, and there have been numerous estimates of the sea-air flux of DMS [e.g., *Barnard et al.*, 1982; *Nguyen et al.*, 1983; *Bates et al.*, 1987; *Erickson et al.*, 1990]. However, recent evidence suggests that the atmospheric loss of DMS may be a relatively minor removal pathway for this compound in the

Paper number 95JC03624.
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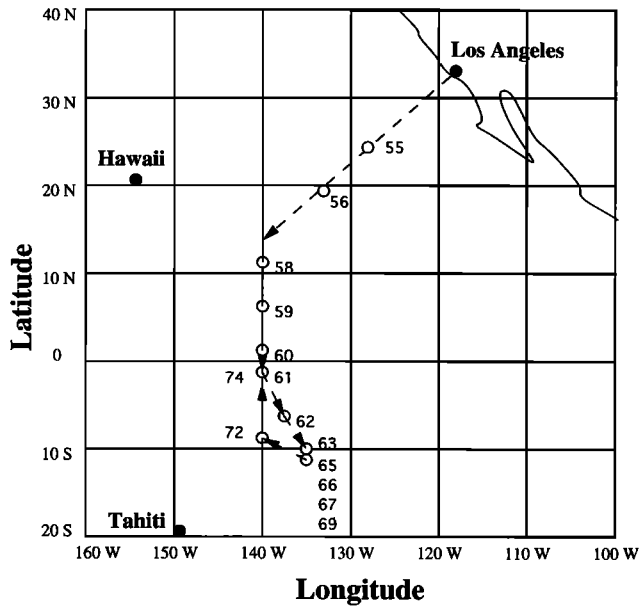

Figure 1. Cruise track for the 1992 International Global Atmospheric Chemistry project's Marine Aerosol Gas Exchange expedition aboard the R/V *Vickers*. Sampling locations are indicated by the open circles. Sampling dates (Julian Day) are given next to each sampling location. Station 2, which was occupied for several days, is located at 12°S 135°W.

upper ocean. In particular, it was recently demonstrated that biological consumption was the predominant removal pathway for DMS when compared to atmospheric losses in the equatorial and northeastern Pacific Ocean [*Kiene and Bates*, 1990; *Bates et al.*, 1994]. By contrast, it has been shown that the chemical oxidation of DMS in seawater is quite slow, with a half-life of the order of years [*Shooter and Brimblecombe*, 1989]. Consequently, the thermal breakdown of DMS will have a negligible effect on its concentration in the upper ocean. This is not the case for the photochemical oxidation of DMS. The photolysis of DMS is considerably faster, occurring on a timescale of days [*Brimblecombe and Shooter*, 1986], and it may be important in the removal of DMS in the photic zone. However, it has not been possible to assess the relative importance of photolysis in the dynamics of the DMS cycle in the photic zone, because no study has been undertaken to determine the magnitude of various removal pathways in the same seawater samples, especially in an open ocean setting.

Here we show that the photolysis of DMS in the equatorial Pacific Ocean proceeds at significant rates at ambient DMS concentrations and light levels. Furthermore, we show that the photochemical turnover rate constants for DMS are comparable to turnover rate constants for atmospheric ventilation and biological consumption. The findings of our study are noteworthy because they establish the importance of photolysis in the oceanic DMS cycle.

Experimental Methods

Chemicals. Anhydrous DMS and dimethylsulfoxide (DMSO) were purchased from Aldrich (Milwaukee, Wisconsin), DMSP hydrochloride was purchased from Research Plus (Bayonne, New Jersey), distilled-in-glass acetonitrile was purchased from Burdick and Jackson (Muskegon, Michigan), and reagent grade sodium hydroxide and hydrochloric acid were purchased from Fisher (Pittsburgh, Pennsylvania). All chemicals were of the highest purity available and used without further purification. Water used in this study was from a Millipore purification system that included filtration/dechlorination, followed by a Milli reverse osmosis (RO) system and a four cartridge Milli Q system, with final filtration through a 0.2 μm Whatman POLYCAP AS capsule (Fisher). This water will subsequently be referred to as Milli Q water.

A 10 m*M* aqueous stock solution of DMS was made in a 25-mL serum bottle with no headspace and capped with a Teflon-lined silicone septum. This stock solution was stable for over 2 months when stored at 4°C. A secondary, aqueous stock solution (~2 μM) was prepared weekly in a 25-mL, capped serum bottle with no headspace and stored at 4°C. Stock solutions of DMS were calibrated using a DMSP standard according to a procedure similar to that described by *Turner et al.* [1990]. Briefly, a 10 m*M* primary standard of DMSP was prepared in a 25-mL serum bottle that was capped with a Teflon-lined butyl rubber septum; this solution was stored frozen when not in use. An aliquot (~25 μL) of this standard was placed in a second serum bottle that contained 25 mL of 0.6 *M* NaOH. The bottle was capped (no headspace) and left overnight to hydrolyze the DMSP to DMS. This secondary standard was then used to generate a standard curve to calibrate the DMS stock solutions previously described.

Sampling. We participated in a research cruise aboard the R/V *Vickers* in the equatorial Pacific Ocean during February–March 1992, as part of the International Global Atmospheric Chemistry project's Marine Aerosol and Gas Exchange (IGAC-MAGE) program. The ship occupied several stations along the transect shown in Figure 1. The most extensive data set was collected at station 2 on Julian Days 65–69. As used in this paper, the Julian Day calendar starts on January 1 (day 1) and proceeds consecutively to December 31 (day 365, except for leap year). Seawater samples were collected for biological consumption and photolysis rate experiments from either the ship's bow intake system at 0600 hours local time, or from 10-L Niskin bottles mounted on a conductivity-temperature-depth rosette; all samples used for these rate studies were collected at 5 m. On the basis of experiments that were periodically conducted, it was observed that rates of microbial uptake and photolysis of DMS in seawater collected from the bow intake system were the same (within an analytical uncertainty of ±10%) as rates determined with seawater from Niskin bottles. Samples for photolysis experiments were collected in 4-L Qorpak bottles with Teflon-lined caps (Fisher, King of Prussia, Pennsylvania). Unless noted, all glassware and plasticware used in the photochemical studies were cleaned prior to use by first soaking in a 10% HCl solution overnight followed by copious rinses with acetonitrile and Milli Q water. Teflon bottles used to collect seawater for biological consumption studies were rinsed with 10% HCl followed by Milli Q water. All sampling bottles were copiously rinsed with the seawater sample just prior to filling.

Analyses were determined according to published procedures that included DMS and DMSP [*Kiene and Service*, 1991] and DMSO [*Kiene and Gerard*, 1994]. These methods were modified slightly with respect to the hardware employed. Analyses were accomplished using a Shimadzu GC-14A gas chromatograph equipped with a flame photometric detector and a CR501 Chromatopac integrator. The column used was a Supelco 245 × 0.32 cm Teflon FEP column (2 mm ID) filled in

the central 183 cm with Chromosil 330 packing (Bellefonte, California). Separations were performed isothermally at an oven temperature of 60°C and detector temperature of 175°C and a carrier gas (He) flow rate of 60 mL min^{-1}.

Deckboard irradiation experiments. Seawater samples were gravity-filtered (Whatman GF/F) into 2-L polycarbonate bottles, which were cleaned as previously noted except that no acetonitrile was used. We periodically observed that DMS accumulated in seawater that was recently filtered through GF/F or 0.2 μm membrane filters. This gave rise to variable results in photolysis experiments. There are several reports of DMS accumulation in freshly collected seawater, presumably due to the enzymatic hydrolysis of DMSP [*Turner et al.*, 1988; *Kiene*, 1990]. Therefore a prefiltration/storage approach was adopted. Samples were incubated in the dark ($\geq$1 day at 4°C) to deplete the dissolved DMSP concentration. Samples were subsequently vacuum filtered (<100 mm Hg) through a 0.2 μm nylon filter (Fisher) and reaerated in a polycarbonate bottle by vigorous stirring. Subsamples were poured into 125-mL Qorpak bottles followed by μL additions of a 10 m*M* aqueous DMS standard to yield a final concentration of DMS in the seawater ranging from 1 to 260 n*M*. After gentle mixing, each sample was poured into a 50-mL quartz flask (Quartz Scientific, Inc., Fairport Harbor, Ohio) and stoppered with no headspace. All sample filtrations, reaerations, and DMS additions were performed on the ship's bow section, with steady head winds (>7.8 ms^{-1}), to minimize potential contamination from organics in the laboratory or from the ship's stacks. Quartz flasks were placed in a shallow, surface-seawater bath (designed to preclude shading) and exposed to sunlight for a fixed solar flux of 0.3 W h cm^{-2} (3–5 hours of exposure depending on the cloud cover). The total light flux was determined with an International Light Corporation model 1700 radiometer (Newburyport, Massachusetts) fitted with a calibrated broadband silicon detector (SUD 038), quartz diffuser, and neutral density filter. However, in order to make comparisons of data, DMS photolysis rates are expressed in units of n*M* h^{-1}. Rate data can be given with respect to the light flux by the appropriate conversion factor. For example, to estimate light-dependent photolysis rates for deckboard irradiation studies, the rate data (n*M* h^{-1}) is multiplied by an average irradiation time of 4 hours and then divided by the solar flux (0.3 W h cm^{-2}).

A bottle comparison study was conducted to determine if the photolysis of DMS in the quartz flasks was an artifact resulting from surface catalyzed reactions on the walls of the flask. For this study a 22 n*M* DMS solution was prepared in a 2-L Qorpak bottle using seawater collected at station 2. This solution was subsampled into triplicate 50-mL quartz round bottom flasks, 250-mL cylindrical FEP Teflon Nalgene bottles (Fisher), and 150-mL square Polycarbonate Nalgene bottles (Fisher). The containers were rinsed, filled, and capped with no headspace and irradiated in the deck water bath for a total light flux of 0.38 W h cm^{-2} (4.5-hour irradiation). The approximate UVB or UVA cutoff for the different vessels, as determined from transmission spectra, was 310 nm for the FEP Teflon, 340 nm for the polycarbonate, and none for the quartz.

Laboratory photochemical studies. Laboratory irradiation studies were performed with stored seawater samples that were collected during the R/V *Vickers* cruise. These samples were filtered (0.2 μm) and stored at 4°C in 20-L fluorinated, high-density polyethylene Jerricans (Fisher).

The wavelength dependence for the photolysis of DMS in the Pacific Ocean samples was determined employing a 1000 W Xe lamp system with monochrometer selected for a 10 nm bandwidth (Spectral Energy, Westwood, New Jersey). Samples were irradiated for 10–150 min in a thermostated (25°C), 1-cm stoppered cell with continuous stirring. A 295 nm cutoff pyrex filter was placed before the cell for all irradiations greater than 360 nm. The light flux was determined by ferrioxalate actinometry [*Hatchard and Parker*, 1956; *Rabek*, 1982] and radiometry. For all wavelengths examined, the initial rate of DMS photolysis was determined (<10% loss) at an initial DMS concentration of 20 n*M*. The light intensity in the cell ranged from 0.26 to 1.30 mW cm^{-2}, depending on the wavelength band considered.

Laboratory kinetic studies were performed with a 300 W Xe lamp system (ILC Technology). The light from the lamp was filtered through 15 cm of Milli Q water followed by a 295 nm cutoff pyrex filter (25% transmission at 340 nm). The light intensity at the cell surface, as determined by the ILC 1700 radiometer, was 445 mW cm^{-2}. A high light intensity was used in this study (approximately 7 suns) to obtain an appreciable loss of DMS for kinetic analysis (~80% in 9 hours). Samples were irradiated in a 1-cm stoppered cell at 25°C with continuous stirring. The initial DMS concentration in these experiments was typically 20 n*M*.

Determination of the production of DMSO from DMS was accomplished by irradiating a 50 n*M* DMS solution in seawater. At this initial DMS concentration, first-order kinetics were observed, and we were able to detect DMSO, even though it was only a minor product. Samples were irradiated in the 300 W Xe lamp system with a 1-cm cell setup, as previously described. The light intensity at the cell surface was 680 mW cm^{-2} (approximately 10 suns). Samples were irradiated from 0.5 to 4 hours. The seawater used in this study was collected on Julian Day 74. A 20 n*M* DMSO light control in seawater (no DMS added) was also examined to determine if there was photochemical loss of this compound under the irradiation conditions employed.

Turnover rate constant determinations. Turnover rate constants k_τ (where k_τ equals turnover $time^{-1}$) were determined for biological consumption, photolysis, and the sea-air flux to assess the relative importance of each pathway in the removal of DMS from the surface mixed layer. Values of k_τ were determined over three depth intervals (0–1 m, 0–20 m, 0–60 m). To simplify calculations, it was assumed that the DMS concentration was uniform within the 60-m mixed layer (vide infra).

The turnover rate constant for atmospheric ventilation was calculated by dividing the sea-air flux by the column-integrated DMS concentration (column burden) for each depth interval considered. The sea-air flux of DMS was calculated from the product of the surface DMS concentration (μmol m^{-3}) and the transport velocity (m d^{-1}), which were obtained using measured DMS concentrations, seawater temperatures, local wind speeds, the diffusivity of DMS in seawater, and an empirically derived transport velocity [*Wanninkhof*, 1992]. The sea-air flux was determined for each surface (5 m) DMS concentration measurement and then averaged over 24 hours ($n \geq 36$). Surface DMS concentrations were measured approximately every 15 min using an automated analysis system plumbed into the ship's bow pumping system; DMS concentrations determined in water from the pumping system agreed quite well (±10%) with DMS concentrations determined in discrete water samples collected in Niskin bottles. Observed differences are close to the uncertainty of the method. The DMS gas diffusivities were taken from *Saltzman et al.* [1993] and reduced by 6% to correct for seawater [*Jahne et al.*, 1987]. Uncertainties associated with the flux measurements are dis-

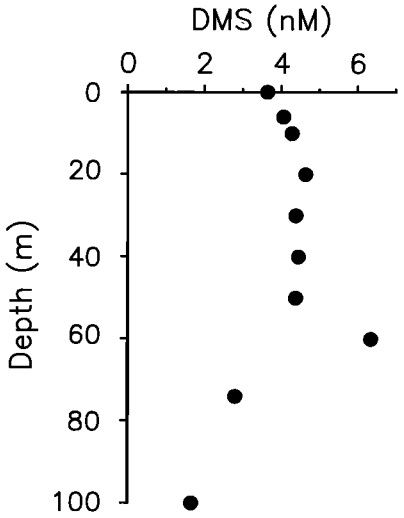

Figure 2. Depth profile of DMS concentrations at station 2 on Julian Day 67. The 0 meter sample was collected just below the sea surface in a Niskin bottle on the conductivity-temperature-depth rossette.

cussed by *Wanninkhof* [1992] and are primarily associated with inherent uncertainties in wind speed/transfer velocity relationships. Using the recommendations of *Wanninkhof* [1992] for sampling frequency and data averaging, we estimate an uncertainty in the flux measurements of ±50%.

The biological k_τ was calculated from the biological consumption rate, as determined by the chloroform inhibition technique [*Kiene and Bates*, 1990; *Bates et al.*, 1994]. Water samples were collected at 0600 local time with 250 mL Teflon bottles and subsequently incubated in the dark at the in situ temperature. Experimental bottles were treated with 500 μM chloroform. The difference in the DMS accumulation rate between the $CHCl_3$-treated samples and those receiving no addition was taken as an estimate of the DMS consumption rate. The biological k_τ was then calculated by dividing the biological consumption rate by the initial DMS concentration in the bottles. Some variations in DMS turnover rate constants with depth in the mixed layer are expected but have been found in other studies to be relatively small [*Kiene*, 1992; *Bates et al.*, 1994]. Therefore in the absence of detailed measurements of biological turnover with depth, we assumed that the rate measured at the surface was constant with depth. Apart from this assumption the uncertainty in determination of k_τ for biological consumption mainly originates from two sources, both related to the chloroform inhibition technique. The first is the uncertainty associated with estimation of slope differences in the time plots of the accumulation of DMS with and without added chloroform. A reasonable estimate for this uncertainty is 30%–50%. The other uncertainty results from the possible release of DMSP and overproduction of DMS due to the addition of chloroform. This may result in an overestimation of DMS consumption rates by as much as 100%–200% [*Wolfe and Kiene*, 1993]. However, this potential bias in the results will not substantially alter our conclusions (see discussion).

The photochemical k_τ was calculated by dividing the depth-averaged photolysis rate by the average, mixed layer DMS concentration determined at 0600 local time. For these calculations the depth-averaged photolysis rate was obtained as follows. First, the sea surface DMS photolysis rate was determined from the product of the first order rate constant (h^{-1}), the 0600 hour DMS concentration, and a conversion factor (8 h d^{-1}). This conversion factor is our conservative estimate for the total amount of time that DMS will undergo photolysis per day. Once the surface rate was obtained, the depth-averaged photolysis rate was determined by taking the average of the predicted photolysis rates (R) that were computed every 0.1 m over the depth interval considered. For this determination we rearranged (1) to solve for R.

We calculated the predicted, fractional photolysis rate (R/R_0) from the following expression:

$$R/R_0 = e^{-Kz} \quad (1)$$

where R_0 is the surface rate determined through deckboard irradiations, R is the rate at depth z, and K is the total diffuse attenuation coefficient for downward irradiance (m^{-1}). Equation (1) was taken from *Smith and Baker* [1979] and modified to reflect that the decrease in R will be equal to the decrease in the downward spectral irradiance with depth in the water column. We assumed that the value of K was constant between 380 and 460 nm at 0.05 m^{-1} [*Smith and Baker*, 1979], which is a reasonable approximation (±20%) for the concentrations of chlorophyll *a* (0.10–0.15 mg m^{-3}) and dissolved organic carbon (DOC) (60–80 μM) that were measured at station 2. The reader is referred to *Smith and Baker* [1979] for information on the variation of K as a function of wavelength at chlorophyll *a* and DOC concentrations representative of different oceanic environments. We also assumed that the concentration of DMS was uniform in the surface mixed layer, as indicated from depth profiles (Figure 2), and that the concentration of absorbing organic matter was well mixed in the surface 60 m.

The uncertainty in the photochemical flux estimates is primarily due to simplifications associated with (1). In particular, in the absence of available underwater irradiance data, we assumed a constant value for K based on the work of *Smith and Baker* [1979]. We estimate that this will result in an error of ±30%, based on the DOC and chlorophyll *a* levels and the wavelengths that were considered. The errors associated with the surface photochemical measurements result from changes in the intensity of sunlight as it passes through the quartz vessels due to reflection, refraction, and scattering. We minimized scattering of light back into the quartz vessels by placing them in a surface seawater bath with a black base. Nonetheless, the quartz vessels will change the light field (relative to uncontained seawater), but the effect is relatively small (~10%).

Results and Discussion

The photolysis of DMS in deckboard irradiated samples followed pseudo first-order kinetics at concentrations less than approximately 50 ± 15 nM. At higher concentrations the photolysis of DMS approached zero-order kinetics (Figure 3a). We confirmed the first-order kinetic loss of DMS in the laboratory, where the photolysis of 20 nM DMS (in Pacific Ocean seawater) was followed to 75% completion (Figure 3b). No loss was observed in dark controls. As another control, we determined that the rates of DMS photolysis in quartz flasks were similar (<25% difference) to rates observed in Teflon or polycarbonate bottles, which was good evidence that the observed DMS loss was not an artifact resulting from photochemical reactions on the wall of the quartz flask (Figure 4). Slight differences that were observed probably reflected differences in the geometries of the containers that were examined.

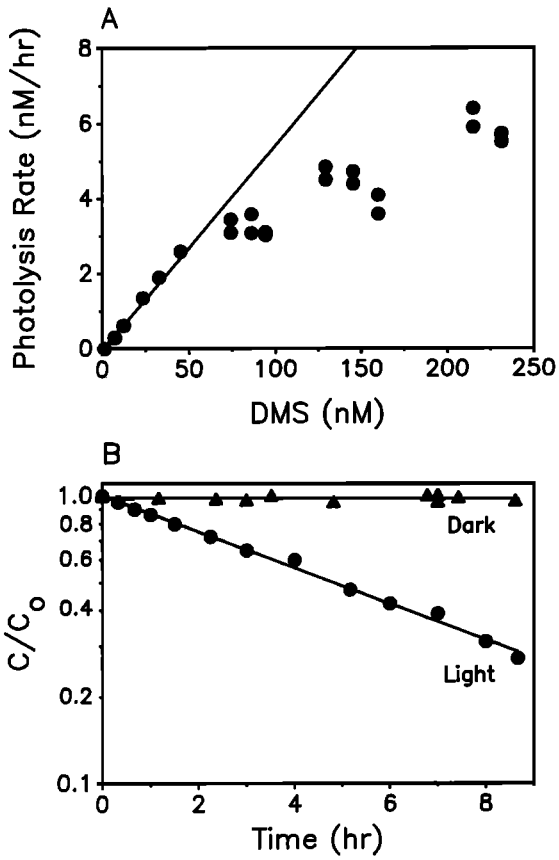

Figure 3. (a) Initial rate of DMS photolysis plotted as a function of the initial DMS concentration in seawater collected on Julian Day 74. Initial rates were determined by deckboard irradiations. The solid line is the least squares fit of the data ≤50 n*M* DMS; the slope is equal to the pseudo first-order rate constant (0.054 ± 0.002 h^{-1} (±SE), with r^2 = 0.967). (b) Semilog plot of C/C_0 as a function of irradiation time is shown by solid circles. The dark control is depicted by solid triangles. C_0 is the initial DMS concentration and C is the DMS concentration measured during the irradiation. Irradiations were performed with the 300 W Xe irradiation system; irradiation conditions are given in the text. The initial DMS concentration was 20 n*M*. For the light exposed sample the pseudo first-order rate constant derived from the slope (±SE) of the best fit line was 0.145 ± 0.003 h^{-1}, with r^2 = 0.997.

Presumably, the observed light-dependent removal of DMS occurs through a secondary photochemical pathway, since DMS does not absorb solar radiation that enters the oceans. However, this secondary pathway(s) does not appear to primarily involve singlet oxygen as previously suggested [*Brimblecombe and Shooter*, 1986]. On the basis of singlet oxygen quencher experiments with sodium azide (data not shown) and experiments where DMSO was measured, we determined that only 14% of the DMS photolyzed through this pathway (Figure 5). The relatively low conversion of DMS to DMSO was not due to losses of DMSO. The DMSO, in a 20 n*M* light control, did not photolyze during the 4-hour irradiation. We are currently investigating other potential mechanisms for the photolysis of DMS in seawater. Despite the low yield, DMSO concentrations in surface waters along the cruise track were correlated (r^2 = 0.507) to DMS photolysis rates obtained for those same waters (Figure 6). For all sampling locations,

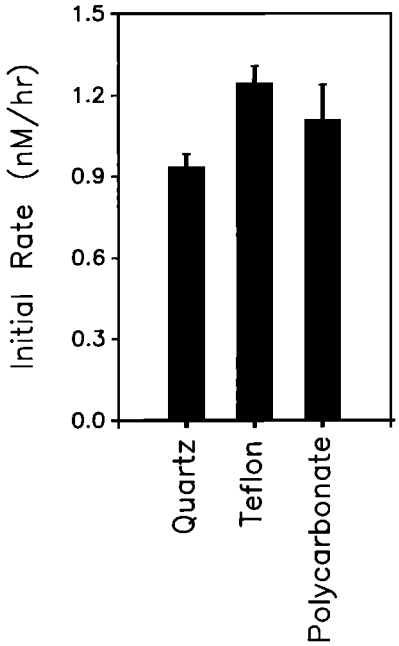

Figure 4. Bottle comparison study. Initial rate of DMS photolysis for three different reaction vessel types. Error bars indicate the 95% confidence interval (n = 3). The initial DMS concentration was 22 n*M*.

DMSO concentrations were 3 to 5 times greater than DMS concentrations (R. P. Kiene et al., manuscript in preparation, 1996). If DMS photolysis is the primary source of DMSO in the open ocean, then our results suggest that the turnover of DMSO in the surface mixed layer is relatively slow (τ > 50 days). Detailed results of DMSO distributions will be presented elsewhere (R. P. Kiene et al., manuscript in preparation, 1996).

Laboratory experiments were conducted on stored, filtered samples to determine the wavelength dependence of the DMS photolysis rate. Maximal rates were observed in the UVB and between 380 and 460 nm (Figure 7a). No DMS loss was observed in dark controls. We used this rate data, along with

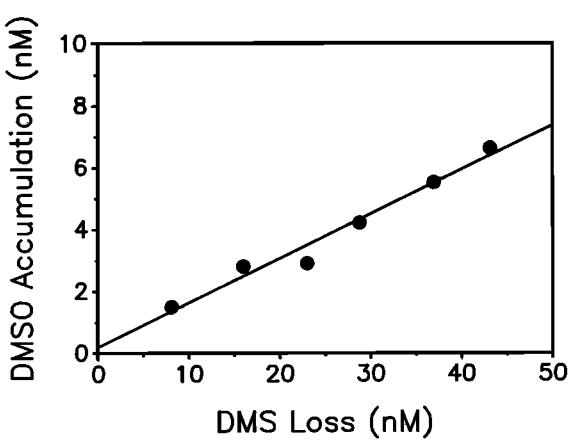

Figure 5. Plot of the concentration of DMSO formed as a function of the concentration of DMS lost during its photolysis in seawater. The least squares fit of the data yielded a slope (±SE) of 0.14 ± 0.01 (i.e., 14% of the DMS was converted to DMSO). The initial DMS concentration was 50 n*M*. The irradiation conditions are given in the text.

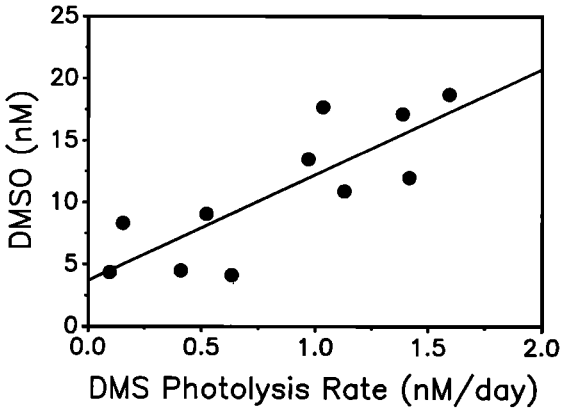

Figure 6. Sea surface DMSO concentrations in the equatorial Pacific plotted versus the daytime DMS photolysis rate determined from deckboard irradiations. The solid line represents the linear regression fit of the data. The slope (±SE) and r^2 are 7.7 ± 2.5 days and 0.507, respectively.

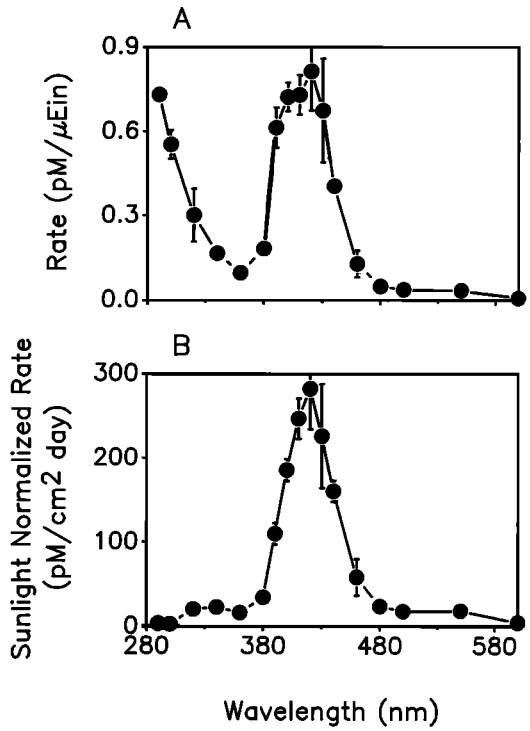

Figure 7. (a) Initial photolysis rate of DMS plotted as a function of wavelength for seawater collected at station 2. The photolysis rates were calculated assuming first-order kinetics and a typical seawater DMS concentration of 2 n*M*. These calculations were based on irradiations with an initial DMS concentration of 20 n*M* for all wavelengths examined. Error bars indicate the 95% confidence interval. (b) Plot of the sunlight-normalized DMS photolysis rates as a function of wavelength is shown. The DMS photolysis rates shown in Figure 7a were normalized to the average springtime solar irradiance incident at the sea surface for 10°S averaged over 10 nm bandwidths [*Leifer*, 1988]. The DMS concentration used for this calculation was 2 n*M*.

average springtime solar irradiance data [*Leifer*, 1988], to calculate the sunlight normalized photolysis rate for DMS in the equatorial Pacific Ocean at station 2. From this calculation it is clearly seen that the photolysis of DMS in seawater occurs predominantly between 380 and 460 nm, with negligible activity in the UVB (Figure 7b). This trend is similar to that observed for other seawater samples from other oceanic regimes (e.g., Gulf of Mexico and Vineyard Sound, Massachusetts) (D. J. Kieber and J. Jiao, manuscript in preparation, 1996), and it is a trend that is consistent with photolysis experiments using polycarbonate bottles with a 340 nm cutoff (i.e., DMS photolysis rates in these bottles were within 15% of the rates observed in quartz flasks, Figure 4). This finding is significant because it establishes that the photolysis of DMS will not be limited to the upper few meters in an open ocean environment. To illustrate this point, we plotted the fractional photolysis rate as a function of depth at station 2 (Figure 8). On the basis of this plot, we predict that the photolysis of DMS will occur throughout the mixed layer (~60 m), with the rate at the base of the mixed layer approximately 5% of the surface value.

The importance of photolysis as a removal mechanism for DMS in the water column was determined through comparison of turnover rate constants. Turnover rate constants were determined using flux data presented in Table 1. A comparison of turnover rate constants was made for three depth intervals (0–1 m, 0–20 m, and 0–60 m) to highlight the importance of all three removal pathways, as shown in Figure 9. The comparisons that are made here are interpreted qualitatively due to the uncertainties associated with some of the assumptions/measurements. For example, the diurnal and depth variability in the rate of biological consumption is not well constrained. Also, in some cases, the chloroform technique may overestimate the biological k_τ by as much as 100% to 200% [*Wolfe and Kiene*, 1993]. Despite these limitations, rate constant comparisons yielded some very interesting trends.

Atmospheric ventilation was the predominant removal pathway for DMS when only the upper 1 m of the water column was considered (Figure 9a), with k_τ ranging from 0.90 to 11.7 d^{-1}. In contrast, values of k_τ for biological consumption and photolysis were much lower ranging from 0.04 to 0.66 d^{-1} and 0.16 to 0.47 d^{-1}, respectively. Atmospheric ventilation was highest early in the study when average winds were greater than 10 m s^{-1} (Julian Days 59–63). The lowest rate constant for atmospheric ventilation corresponded to the calmest day of this study when the average wind speed was 5.6 m s^{-1} (Julian Day 74). During this time, photolysis of DMS was comparable to the atmospheric flux in the removal of DMS from the upper meter of the water column.

As may be expected, the importance of atmospheric ventilation decreases when a deeper water column is considered, since sea-air exchange only occurs at the sea surface. For the upper 20 m the atmospheric removal rate constant varied from 0.05 to 0.58 d^{-1} (Figure 9b), which is appreciably lower than observed at the surface. By comparison, biological consumption and photolysis turnover rate constants were comparable ranging from 0.04 to 0.66 and 0.11 to 0.30 d^{-1}, respectively. Thus all three removal processes are important over this depth range, with no single process consistently governing the DMS loss. When this comparison is extended to the entire mixed layer (~60 m), biological consumption frequently was the predominant removal pathway for DMS (Figure 9c). Biological turnover rate constants were a factor of 3 to 11 greater than either photolysis or sea-air exchange on Julian Days 59, 61, 63, and 66. This trend was not always observed, however, contrast-

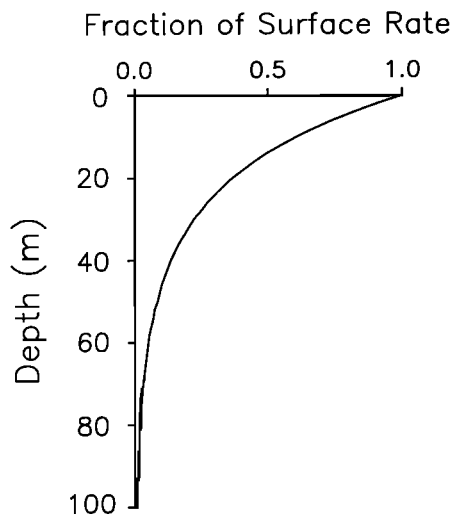

Figure 8. The fraction of the surface DMS photolysis rate plotted as a function of depth at station 2.

ing previous reports where biological consumption largely controlled (~95%) the loss of DMS in the mixed layer [*Kiene and Bates*, 1990; *Bates et al.*, 1994]. It should be noted that photolysis was not considered in either of these studies. Our results can be explained on the basis of the higher average wind speeds and lower biological consumption rates that we observed compared to previous studies. In particular, on Julian Days 67 and 69 each removal mechanism accounted for a significant percentage of the total DMS loss, and on Julian Day 62, when the biological consumption rate was quite slow (0.2 nM d^{-1}), photolysis and atmospheric ventilation controlled the loss of DMS in the mixed layer. On the basis of these findings, we suggest that the photolysis of DMS is quite important in the removal of DMS in the upper water column in this region, as it accounts for 7% to 40% of the total removal of DMS from the mixed layer. When photolysis is included in the determination of the turnover time for DMS, we found that DMS was turned over rapidly, from 1 to 4 days, which was considerably shorter, in some cases, than if only biological consumption was considered (e.g., the biological turnover time ranged from 1 to 25 days).

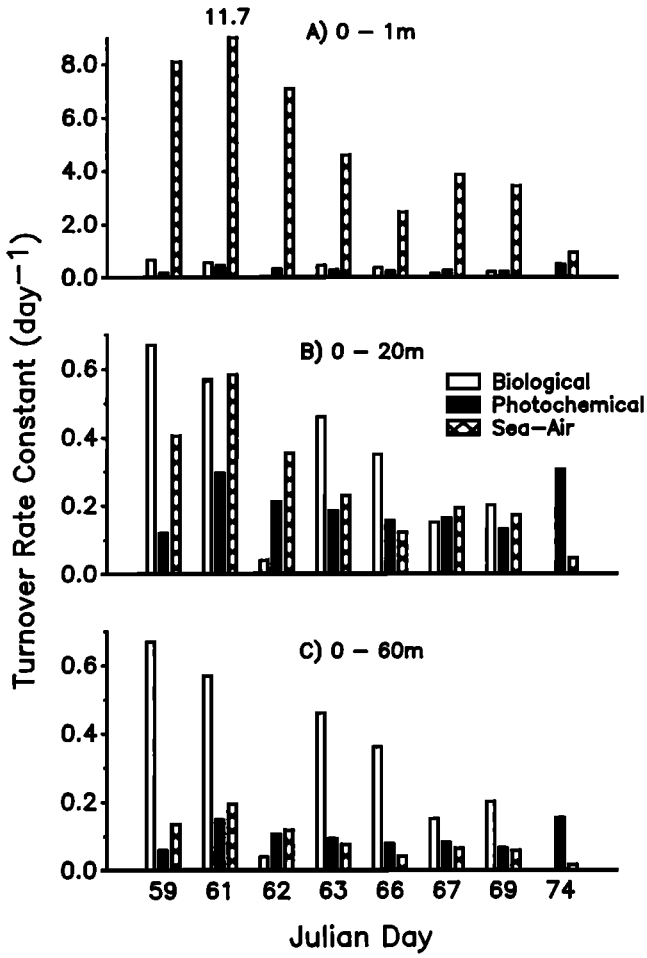

Figure 9. Comparison of the DMS turnover rate constant for photochemical, biological, and sea-air exchange processes. Three depth intervals were considered: (a) 0–1 m, (b) 0–20 m, and (c) 0–60 m.

The notion that DMS undergoes photochemical degradation in seawater is not new. *Brimblecombe and Shooter* [1986] showed that DMS photolyzed in seawater collected from the North Sea at rates that suggested an important role for this process in the marine DMS cycle. Our results not only confirm

Table 1. Removal Rates of Dimethylsulfide in Surface Seawater Through Its Photolysis, Biological Consumption, and Sea-Air Flux

Julian Day	[DMS], nM	Photolysis Rate, nM d^{-1}	Biological Consumption, (nM d^{-1})	DMS Column Burden, μmol m^{-2}			Wind Speed, m s^{-1}	Sea-Air Flux, μmol m^{-2}d^{-1}
				1 m	20 m	60 m		
58	3.0	0.5	...	3.0	60	180	8.9	20
59	2.1	0.4	1.4	2.1	42	126	11.3	17
60	1.5	0.6	...	1.5	30	90	12.2	14
61	3.0	1.4	1.7	3.0	60	180	11.4	35
62	4.8	1.6	0.2	4.8	96	288	12.0	34
63	4.8	1.4	2.2	4.8	96	288	10.1	22
65	4.2	1.0	...	4.2	84	252	7.8	16
66	4.5	1.1	1.6	4.5	90	270	6.9	11
67	3.9	1.0	0.6	3.9	78	234	7.2	15
69	4.4	0.9	0.9	4.4	88	264	6.6	15
74	3.3	1.6	...	3.3	66	198	5.6	3

Reported wind speeds are 24-hour averages. The dimethylsulfide (DMS) concentrations depicted were determined at 0600 hours local time. Dots indicate there were no data. Photolysis rates are based on an 8-hour photoperiod.

their initial findings but, more importantly, extend them to natural light levels, oligotrophic conditions, and ambient DMS concentrations. We conclude that the photolysis of DMS is likely to be a significant, and at times, a major sink for DMS in oligotrophic surface waters. This finding is important because factors that control the concentration of DMS in surface waters will indirectly affect global climate and atmospheric chemistry.

Acknowledgments. This work was supported by the Ocean Chemistry Program of the Office of Naval Research (ONR-N00014-91-J4003, D.J.K.), the National Science Foundation (OCE92-03728, R.P.K.), and the Climate and Global Change Program of the National Oceanic and Atmospheric Administration (T.S.B.) and is a contribution to the International Global Atmospheric Chemistry (IGAC) Core Project of the International Geosphere Biosphere Programme (IGBP). Funding was also provided by the Summer Visiting Scientist Program at the University of Georgia Marine Institute, Sapelo Island, Georgia (D.J.K.). Thanks are extended to Ronald Benner (University of Texas at Austin) for providing the DOC results.

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(Received February 20, 1995; revised July 1, 1995;
accepted November 6, 1995.)