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The cycling of sulfur in surface seawater of the northeast Pacific

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Abstract. Oceanic dimethylsulfide (DMS) emissions to the atmosphere are potentially important to the Earth's radiative balance. Since these emissions are driven by the surface seawater concentration of DMS, it is important to understand the processes controlling the cycling of sulfur in surface seawater. During the third Pacific Sulfur/Stratus Investigation (PSI-3, April 1991) we measured the major sulfur reservoirs (total organic sulfur, total low molecular weight organic sulfur, ester sulfate, protein sulfur, dimethylsulfoniopropionate (DMSP), DMS, dimethylsulfoxide) and quantified many of the processes that cycle sulfur through the upper water column (sulfate assimilation, DMSP consumption, DMS production and consumption, air-sea exchange of DMS, loss of organic sulfur by particulate sinking). Under conditions of low plankton biomass (<0.4 μg/L chlorophyll *a*) and high nutrient concentrations (>8 μM nitrate), 250 km off the Washington State coast, DMSP and DMS were 22% and 0.9%, respectively, of the total particulate organic sulfur pool. DMS production from the enzymatic cleavage of DMSP accounted for 29% of the total sulfate assimilation. However, only 0.3% of sulfate-S assimilated was released to the atmosphere. From these data it is evident that air-sea exchange is currently only a minor sink in the seawater sulfur cycle and thus there is the potential for much higher DMS emissions under different climatic conditions.

Introduction

Oceanic dimethylsulfide (DMS) is currently thought to be the major natural source of sulfur to the atmosphere [*Bates et al.*, 1992; *Spiro et al.*, 1992]. Once in the atmosphere, DMS is oxidized to produce aerosol particles which affect the acid-base chemistry of the atmosphere [*Charlson and Rodhe*, 1982] and the radiative properties of marine stratus clouds [*Charlson et al.*, 1987; *Falkowski et al.*, 1992]. This latter effect is calculated to have a major impact on the Earth's radiative balance and hence its climate [*Charlson et al.*, 1987].

The starting point in the marine atmospheric sulfur cycle is the air-sea exchange of DMS which is a function of the gas transfer velocity and surface seawater DMS concentration. The gas transfer velocity is controlled primarily by surface turbulence, seawater temperature and gas diffusivity and can be modeled as a function of wind speed for various trace gases [*Liss and Merlivat*, 1986; *Wanninkhof*, 1992]. The different models produce gas transfer velocities that vary by about a factor of 2 [*Wanninkhof*, 1992]. Unfortunately, the factors controlling oceanic DMS concentrations and the parameters needed to model these concentrations are not nearly as well characterized. Existing data suggest that oceanic DMS concentrations have changed over geological time scales and continue to vary both regionally and seasonally. Ice core measurements of the atmospheric DMS oxidation product, methanesulfonate, suggest that DMS emissions (and presumably oceanic DMS concentrations) may have changed by a factor of 6 between glacial and interglacial times [*Legrand et al.*, 1991]. Seasonal studies of oceanic DMS concentrations [*Bates et al.*, 1987; *Turner et al.*, 1988; *Leck et al.*, 1990; *Nguyen et al.*, 1990; *Berresheim et al.*, 1991] have shown that average surface seawater DMS concentrations can vary by as much as a factor of 50 between summer and winter in the mid and high latitudes. Overall, the concentration of DMS in surface seawater varies from approximately 0.2 n*M* in winter to 10 n*M* in summer. However, DMS concentrations in excess of 90 n*M* have been measured in summer plankton blooms in the North Atlantic [*Malin et al.*, 1993] and Southern Ocean [*Gibson et al.*, 1990; *Fogelqvist*, 1991]. On large regional and temporal scales, DMS concentrations have been correlated with seawater chlorophyll concentrations [*Thompson et al.*, 1990], but in general, oceanic DMS distributions are poorly correlated with phytoplankton production or biomass [*Andreae*, 1986, 1990; *Leck et al.*, 1990]. Part of the difficultly in establishing these correlations is that the production of the DMS precursor, dimethlysulfoniopropionate (DMSP), is highly

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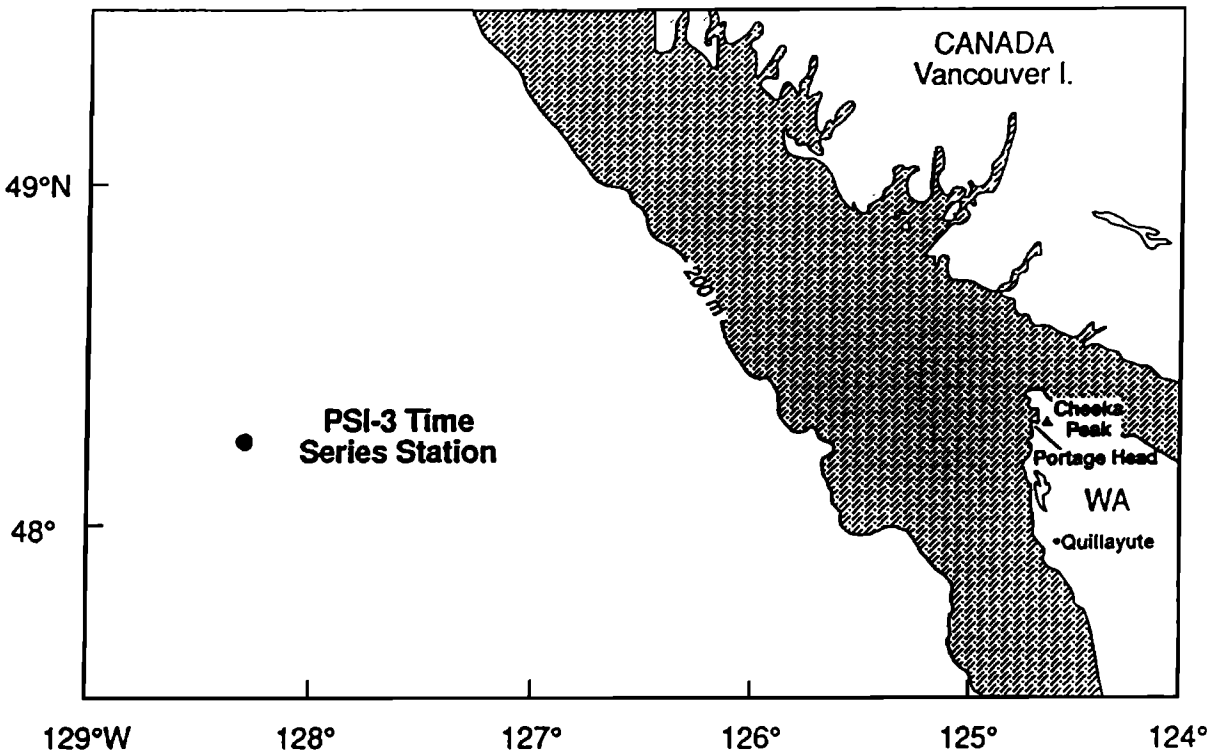

Figure 1. PSI-3 study area off the Washington State Coast showing the location of the sediment trap mooring and the initial location of the time series station (48°14′N, 128°20′W). The station was 250 km from Portage Head in 2600 m of water. During the initial occupation (April 17 at 0600 to April 21 at 0000) the surface mixed layer was tracked with a drogue buoy. CTD casts and water samples were collected every 6 hours. The station was reoccupied twice, on April 26 at 0600–1200 and on April 30 at 1200.

species specific [*Barnard et al.*, 1984; *Holligan et al.*, 1987; *Iverson et al.*, 1989; *Keller et al.*, 1989] and the conversion of DMSP to DMS is often associated with the decline of a phytoplankton bloom during the senescence phase or during active zooplankton grazing as opposed to the active growth phase [*Dacey and Wakeham*, 1986; *Nguyen et al.*, 1988; *Turner et al.*, 1988; *Leck et al.*, 1990]. The other complicating factor is that air-sea exchange appears to be only a small sink for oceanic DMS and instead there exists an active biological sulfur cycle within the ocean surface waters [*Wakeham et al.*, 1987; *Andreae*, 1990; *Belviso et al.*, 1990; *Kiene and Bates*, 1990; *Leck et al.*, 1990; *Kiene*, 1992]. From these data it is apparent that reliable parameterizations of surface oceanic DMS concentrations will require a better understanding of the processes involved in the cycling of sulfur in the upper water column.

As a first step toward quantifying this cycle, we made simultaneous measurements of the key sulfur species and the rates of conversion between these species during the third Pacific Sulfur-Stratus Investigation (PSI-3, April 15–30, 1991). The measurements were conducted at a station in the northeastern Pacific Ocean 250 km off the coast of Washington State (Figure 1) in 2600 m of water. Here we describe the integrated measurements from this station. Further details of the regional planktonic distributions (F. P. Chavez et al., manuscript in preparation, 1994), DMS and DMSP concentrations (G. V. Wolfe et al., manuscript in preparation, 1994) and rates of sulfate assimilation (R. L. Cuhel et al., manuscript in preparation, 1994) will be presented elsewhere.

Methods

Sample Collection

Water samples were collected aboard the National Oceanic and Atmospheric Administration (NOAA) ship *Discoverer* using 10 L acid-cleaned Niskin bottles deployed on a standard rosette with a Neil Brown conductivity-temperature-depth (CTD). The Niskin bottles were modified with silicon O-rings and silicon tubing as the closing mechanism. Sampling casts were conducted in the upper 200 m of the water column every 6 hours while on station. The station was defined by a loran-tracked drifter with a holey-sock drogue that was deployed at the beginning of the experiment. During the course of the experiment the drogue traveled approximately 5 km/d in a northwesterly direction.

Sinking particles were collected with sediment traps deployed at 100, 150 and 200 m on an anchored mooring. The gimbaled traps [*Baker and Milburn*, 1983] were a cylindrical design with a cross-sectional area of 324 cm^2 and a funnel height to width ratio of 3. The particle flux was concentrated at the bottom of the steep-walled funnel, which led to 1 of 10 separate sampling tubes containing 38 n*M* sodium azide and 850 m*M* sodium chloride to reduce microbial degradation. A self-contained sampling mechanism rotated a new tube into position under the funnel every 48 hours. Upon retrieval the tubes were stored at 4°C until subsampled. Due to the small amount of material collected, tubes were combined to give a total of two samples per trap. The "swimmers" (primarily copepods) were picked from the samples by hand and the

remaining material was split volumetrically for various analyses. The tubes containing the azide/salt solution which did not rotate under the funnel were used as blanks.

Particulate Organic Carbon, Nitrogen and Reduced Sulfur Analyses

Water samples (0.5–2.0 L) and sediment trap samples were gently (<5 cm Hg) filtered through precombusted GF/F filters, rinsed (using 3% ammonium formate for sulfur samples), and frozen until analysis. Carbon (PC) and nitrogen (PN) were analyzed on a Control Equipment Corporation CHN analyzer. Reduced sulfur (POS) was analyzed on an Antek sulfur detector [*Matrai*, 1989].

Primary Productivity, Chlorophyll, and Nutrient Analyses

Water samples for determination of simulated in situ carbon productivity were collected at 0, 5, 10, 20, 40 and 60 m. Seawater samples were drawn into 280 mL polycarbonate bottles, spiked with 10 μCi of $NaH^{14}CO_3$, and encased in nickel screens to reduce the light intensity to the same level as that occurring at the depth from which the sample was collected. The samples were incubated in on-deck seawater-cooled Plexiglass incubators. After 24 hours the samples were filtered onto GF/F filters and counted in 10 mL of Cytoscint on board ship [*Chavez et al.*, 1990].

Water samples for the determination of chlorophyll *a* and phaeopigments were filtered onto GF/F filters and extracted with 90% acetone in a freezer for 24 to 30 hours. The extract was analyzed by fluorometry using a Turner Designs 10-005 R fluorometer calibrated with commercial chlorophyll *a* (Sigma). Samples for nutrient analyses were frozen immediately and later analyzed onshore using an Alpkem autoanalyzer [*Chavez et al.*, 1990].

Plankton Speciation and Carbon Determinations

Plankton samples were collected on 0.2 μm pore size Nuclepore filters. Individual phytoplankton and small heterotrophs were sized and counted using epifluorescence microscopy [*Chavez et al.*, 1990]. Cell volumes were calculated from the cell dimensions and phytoplankton carbon was estimated from the volumes using relationships derived from cultures and described in detail by *Chavez et al.* [1991].

Sulfate Assimilation Rate Measurements

Water samples were collected during the daily predawn cast at 0, 5, 10 and 20 m for the determination of sulfate assimilation rates. Samples were spiked with 2.2 mCi of $^{35}SO_4^=$ and incubated in on-deck seawater-cooled Plexiglas incubators with screens to mimic the light levels at the depths of sample collection. After 12 and 24 hours the samples were filtered through GF/F filters, rinsed, and frozen for subsequent laboratory processing. The laboratory analysis included a fractionation sequence [*Cuhel and Lean*, 1987] which subdivided the radiolabeled sulfur into four fractions: a low-molecular weight (LMW) fraction which contained amino acids, peptides, nuceotides, vitamins, coenzymes, sugars, sugar phosphates and presumably DMSP; a protein fraction which included cellular and membrane proteins; a sulfate-ester fraction and a sulfolipid fraction. Only the first two fractions contained reduced sulfur that could be directly compared with the POS measurement.

DMS, DMSP, DMSO Analyses

Seawater DMS and DMSP concentrations were measured using purge and trap gas chromatography with flame photometric detection. The detailed methods have been described previously [*Kiene and Service*, 1991]. Due to inconsistencies in the partitioning of dissolved and particulate DMSP encountered during PSI-3 (G. V. Wolfe et al., manuscript in preparation, 1994), the DMSP data reported here are for total (dissolved and particulate) DMSP. DMS production and consumption rates reported here were obtained by incubating water samples in the dark at in situ temperatures in 250 mL Teflon bottles with 500 μM $CHCl_3$. $CHCl_3$ at this concentration has been shown to inhibit DMS metabolism [*Wolfe and Kiene*, 1993a,b] while allowing continued production. DMS consumption rates were estimated from the difference between the rate of change in DMS concentrations with and without chloroform [*Kiene and Service*, 1991]. Gross DMS production rates were estimated from the absolute rate of increase in DMS concentrations in the presence of chloroform. Incubations of the samples in the dark precluded any photochemical losses of DMS [*Brimblecombe and Shooter*, 1986]. The air-sea exchange of DMS was calculated using ship wind speeds, surface seawater temperatures and the wind speed/gas transfer velocity relationship of *Liss and Merlivat* [1986]. The details of these calculations have been presented previously [*Bates et al.*, 1992].

Seawater dimethylsulfoxide (DMSO) concentrations were measured using isotope dilution gas chromatography/mass spectrometry (GC/MS) [*Ridgeway et al.*, 1992]. Seawater samples were spiked with d_6-DMSO, filtered and adjusted to a *p*H of 13 to convert DMSP to DMS. After 12 hours the samples were purged to eliminate DMS. DMSO was then reduced to DMS using $NaBH_4$. The DMS was purged from the sample and trapped and stored in liquid nitrogen. GC/MS analyses were performed after the cruise.

Results

Physical, Chemical, and Biological Setting

The hydrography off the Washington Coast during the spring includes a northerly coastal flow of relatively fresh water from the Columbia River and Strait of Juan de Fuca confined primarily to the continental shelf (bottom depths <200 m), a southerly offshore flow (California Current) from the subarctic and a counterclockwise flow (Davidson Current) between the two, also from the subarctic [*Hickey*, 1989]. These three current regimes were all evident during PSI-3 (G. V. Wolfe et al., manuscript in preparation, 1994). The time series station, 250 km from shore, was in the northwestward flow region of the Davidson Current as evidenced by the temperature and salinity distributions (Figure 2a) and the drift of the drogue (5 km/d in a northwesterly direction). During the experiment the skies were generally cloudy with winds from the northwest at 8.0 ± 1.6 m/s. These wind and cloud cover conditions maintained the deep winter mixing (Figure 2a) which kept the surface water nutrient concentrations high (>8 μ*M* nitrate, Figure 2b) and the phytoplankton biomass and productivity rates low (chlorophyll *a* < 0.4 μg/L, primary productivity 36 ± 11 mmoles $C/m^2/d$). These values are consistent with the broad-scale distribution of hydrographic, chemical and biological variables off the Washington coast during the winter [*Landry et al.*, 1989; *Perry et al.*, 1989]. The

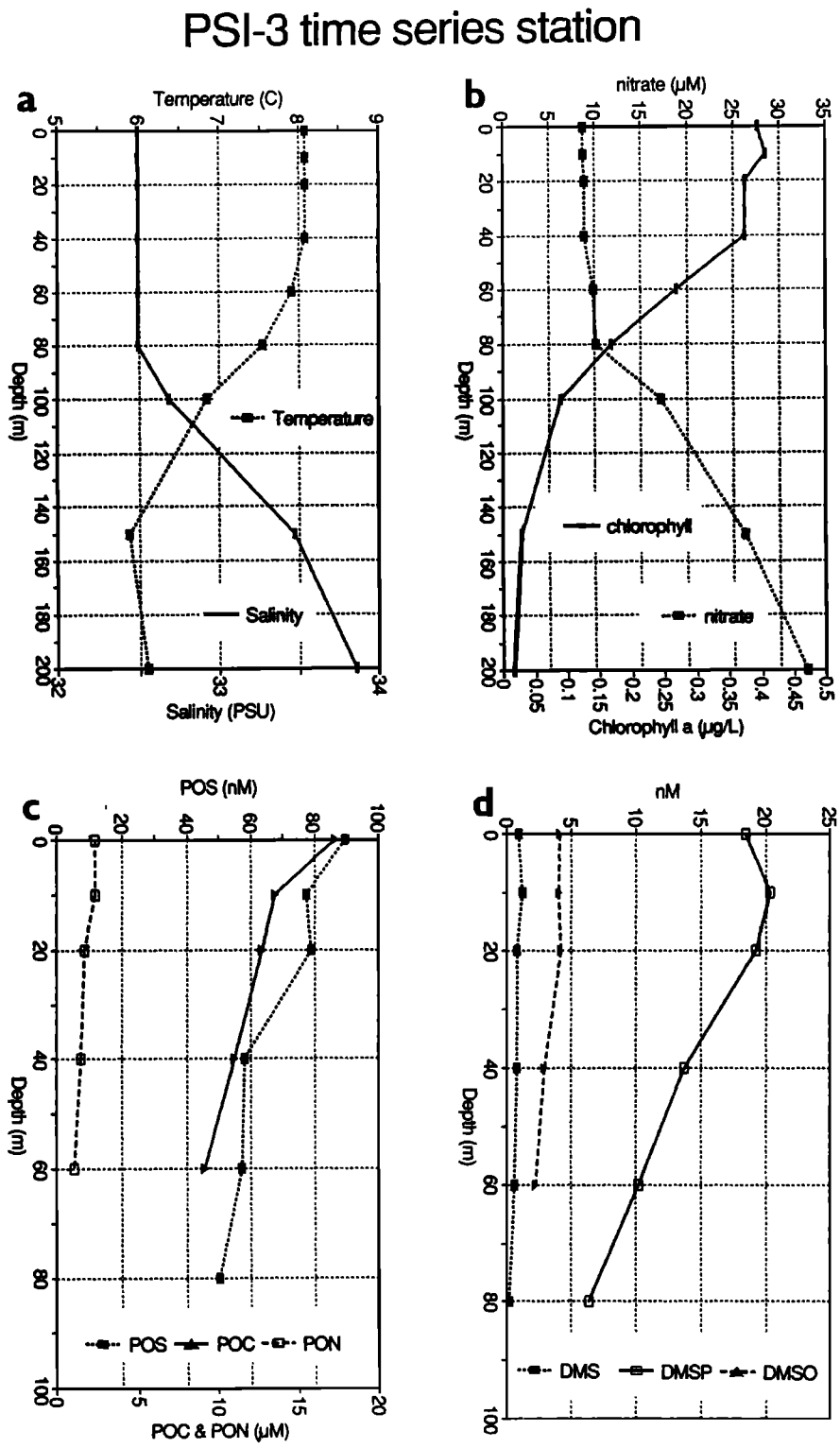

Figure 2. Representative vertical distributions of (a) potential temperature (degrees Celsius) and salinity (practical salinity units), (b) nitrate (micromolar) and chlorophyll *a* (micrograms per liter), (c) PC (micromolar), PN (micromolar), and POS (nanomolar), and (d) total DMSP, DMS, and DMSO (nanomolar) versus water depth (meters) at the time series station. All parameters appeared to be in quasi-steady state during the study.

depth integrated (60 m) plankton carbon biomass, obtained from phytoplankton counts, was approximately 160 mmoles C/m^2 and was dominated by autotrophic picoplankton (56% of the population was smaller than 2 μm and was composed mainly of *Synechococcus* (F. P. Chavez et al., manuscript in preparation, 1994)). The abundance of picoplankton during PSI-3 was higher than the average observed at ocean station PAPA (50°N, 145°W) during May 1984 (28% [*Booth*, 1988]), but in both cases this size class was dominated by *Synechococcus*. Using the exponential growth equation, the plankton

carbon derived from microscope counts and primary productivity rates [*Chavez et al.*, 1991], the growth rate of the phytoplankton population was estimated to be 0.3 doublings per day.

Sulfate Assimilation and the Incorporation of Sulfur Into Organic Compounds

Inorganic sulfate was assimilated into organic sulfur compounds at an average rate of 260 μmoles/m^2/d (R.L. Cuhel et al., manuscript in preparation, 1994). Of the sulfate assimilated, 40% was incorporated into LMW compounds, 35% into proteins, 21% into ester-sulfate, and 4% into lipids. Based on this fractionation, 195 μmoles/m^2/d of sulfate (40 + 35% of the total) was incorporated into reduced LMW compounds and 90 μmoles/m^2/d of this sulfur went on to form proteins.

Elemental Composition of Water Column Particulates

The column integrated burdens (60 m) of total carbon (PC), nitrogen (PN) and reduced organic sulfur (POS) were 820, 120, and 4.5 mmoles/m^2, respectively (Figure 2c). These concentrations correspond to a molar C:N:S ratio of 182:27:1 which, based on carbon and nitrogen, is indicative of a phytoplankton source [*Redfield et al.*, 1963]. The N:S ratio is identical to that obtained by *Matrai and Eppley* [1989] for suspended particulates in waters of the Southern California Bight. In comparison, exponentially growing cells of marine *Synechococcus* incorporate C, N, and S at a ratio of 95:16:1 [*Cuhel and Waterbury*, 1984]. If this ratio is typical of the other plankton species present during PSI-3, it would suggest that the sulfur is more labile than the carbon and nitrogen compounds.

The loss of particulate carbon and sulfur from the water column during PSI-3 via sedimentation (sediment trap samples) was extremely small, averaging only 1.0 ± 0.26 mmoles C/m^2/d and 0.95 ± 0.98 (range 0.18 to 2.65) μmoles S/m^2/d. The lifetime of water column particulate carbon and sulfur with respect to these fluxes would be of the order of years. Although this small loss of carbon and sulfur is consistent with similar measurements in the Gulf of Maine [*Matrai and Keller*, 1993], we consider these values to be lower limits since we cannot rule out decomposition of carbon and sulfur in the traps.

DMS, DMSP, and DMSO Concentrations

DMS, DMSP, and DMSO concentrations were highest in the upper 40 m of the water column (Figure 2d). The average depth-integrated (60 m) concentrations of DMS, DMSP, and DMSO were 40 ± 7 μmoles/m^2, 1000 ± 240 μmoles/m^2, and 200 ± 3 μmoles/m^2, respectively. DMS concentrations in the upper water column (0.75 ± 0.21 nM) were typical of temperate latitude North Pacific winter values [*Bates et al.*, 1987, 1990]. Total DMSP concentrations in the upper water column (18.6 ± 5.8 nM) were much higher than DMS concentrations. On average, 77% of the DMSP was retained on the GF/F filters (G. V. Wolfe et al., manuscript in preparation, 1994). During PSI-3 the partitioning between dissolved and particulate DMSP was very dependent upon filtering techniques, with subtle differences in filtering pressure resulting in large differences in the partitioning. For DMSP we have chosen to report the values as total (dissolved + particulate) DMSP. However, some particulate DMSP was undoubtedly lost from the samples collected for POS and sulfate assimilation determinations. We must consider the POS and sulfate assimilation values therefore as lower limits.

The average total DMSP:DMS ratio at this station (25 ± 8.7) was similar to that found in the northeast Atlantic Ocean during the summer coccolithophore bloom (21 [*Malin et al.*, 1993]) but higher than that found in previous studies (North Sea and English Channel ratio = 8 [*Turner et al.*, 1988]; estuarine and coastal waters of the eastern United States ratio = 3 [*Iverson et al.*, 1989]; central Atlantic Ocean ratio = 3 [*Burgermeister et al.*, 1990]). DMSO concentrations were intermediate between DMS and DMSP concentrations and were similar to those measured off the coast of Maryland by *Ridgeway et al.* [1992].

DMS consumption rates, as determined by the chloroform inhibition technique, were uniform throughout the upper 40 m of the water column (1.0 ± 0.14 μmoles/m^3/d (R. P. Kiene and S. K. Service, manuscript in preparation, 1994)). The depth-integrated consumption rate for the upper 60 m was 50 μmoles/m^2/d. DMS production, estimated from the absolute increase in DMS in the presence of chloroform, was 75 μmoles/m^2/d. Recent studies [*Wolfe and Kiene*, 1993b] suggest that the chloroform inhibition technique may overestimate DMS production rates due to enhanced DMS production in the presence of chloroform. Thus we consider the DMS rate measurements reported here as upper estimates. However, even if these rates are high by a factor of 2, they do not affect the major conclusions of this study.

DMS loss to the atmosphere, based on air-sea exchange model calculations [*Bates et al.*, 1992], was 0.8 μmoles/m^2/d. Based on sediment trap samples, DMSP loss from the upper water column via particulate sinking was minimal, amounting to only 0.0023 ± 0.0013 μmoles/m^2/d.

Discussion

Assuming steady state conditions, the various measurements made during PSI-3 (Tables 1 and 2) can be integrated together to form a conceptual model of the surface ocean seawater sulfur cycle (Figure 3). The oceans are a vast reservoir of sulfur in the form of dissolved sulfate (28 mM). Bacteria and phytoplankton are able to actively assimilate this sulfate to produce the essential organic compounds needed for their survival. Of the total sulfate assimilated at the time series stations during PSI-3, 195 μmoles/m^2/d (75%) were incorporated into reduced organic sulfur compounds with 90 μmoles/m^2/d (35%) of this sulfur being further incorporated into proteins. This left 105 μmoles/m^2/d (40%) of the assimilated sulfate in the form of nonprotein reduced sulfur which would include DMSP-sulfur. The 105 μmoles/m^2/d must be considered a lower limit given the probable loss of DMSP during sample filtration and freezing.

On average, at least 22% of the average depth-integrated reduced organic sulfur burden (POS = 4500 μmoles/m^2) was in the form of DMSP. Thus DMSP can be a major fraction of the total burden of reduced organic sulfur in surface waters. This conclusion is supported by recent laboratory studies of phytoplankton cultures in which DMSP comprised up to 70% of the cellular organic sulfur of some species [*Matrai and Keller*, 1993].

It appears that relatively little intracellular DMSP is degraded to DMS by healthy, growing algal cells [*Wakeham and Dacey*, 1989; *Keller*, 1991]. However, during algal senescence [*Nguyen et al.*, 1988; *Turner et al.*, 1988; *Leck et al.*, 1990] or zooplankton grazing [*Dacey and Wakeham*, 1986;

Table 1. PSI-3 Sulfur Pools

Pool	Number of Casts*	Size, mmol/m^2 (Estimated Uncertainty,† %)	Comments‡
Particulate reduced organic sulfur (POS)	5	4500 (15)	lower estimate due to filtration losses
DMSP (total)	12	1000 (25)	
DMS	12	40 (20)	
DMSO	2	200 (3)	some additional uncertainty due to limited number of samples

* There are 5–8 sample depths per cast.
† Uncertainty estimated as standard deviation of total burden from measured casts.
‡ See text for details.

Leck et al., 1990] the production of DMS from DMSP is accelerated. Although the large burden of DMSP that was present during PSI-3 could potentially have contributed to a large burden of DMS, DMS concentrations were relatively low and typical of mid-latitude winter conditions [*Bates et al.*, 1987]. The implication of these results is that DMSP can be degraded into compounds other than DMS, and/or DMS is consumed more quickly within the upper ocean sulfur cycle.

Based on the average depth-integrated burdens of total carbon (PC) and reduced organic sulfur (POS) and the average rates of carbon fixation and sulfate assimilation, the residence times for PC and POS in the upper water column were both 23 days. This agreement is undoubtedly fortuitous since the relative reactivities of the various carbon- and sulfur-containing compounds vary greatly. In fact, based on the total plankton biomass and the average rate of carbon fixation, the planktonic organic carbon residence time was only 4.4 days. If we assume that the labile particulate sulfur compounds, such as DMSP, have a similar residence time (a conservative estimate since the sulfur is probably more labile than the carbon [*Matrai and Eppley*, 1989]), DMSP must be produced and consumed at a rate of 230 μmoles/m^2/d. Because the gross DMS production rates were estimated to be only 75 μmoles/m^2/d, the remaining 67% of the DMSP must be lost via other processes. These results agree with several recent studies which found that >70% of the dissolved DMSP degradation in estuarine and oceanic waters did not result in DMS formation. Alternative pathways for DMSP metabolism involve demethylation and this has been observed in anoxic sediments [*Kiene and Taylor*, 1988] and more recently in oceanic surface waters [*Taylor and Gilchrist*, 1991; *Visscher et al.*, 1993]. *Belviso et al.* [1990] also suggested that DMSP was demethylated during grazing by microheterotrophs on phytoplankton and bacteria. We were unable to directly measure the fraction of DMSP converted to DMS during PSI-3 due to filtration-induced release of dissolved DMSP in our experiments. Nonetheless, the imbalance in the DMS production and DMSP degradation rates strongly argues that a significant fraction of DMSP is not degraded to DMS. Biological consumption appeared to be the major loss mechanism for DMSP during PSI-3 because vertical advection/diffusion and sedimentation were insignificant and abiological degradation of DMSP is extremely slow at seawater *p*H (half-life on the order of years [*Dacey and Blough*, 1987; *Turner et al.*, 1988]).

DMSP appears to be the major source of DMS in the

Table 2. PSI-3 Sulfur Fluxes

Flux	Method of Calculation	Magnitude, mmol/m^2/d	Comments*
Sulfate assimilation in reduced form	$^{35}SO_4$ uptake onto particles	195	lower estimate due to filtration losses
DMSP turnover	from living carbon turnover time of 4.4 days	230	assumes same turnover time as carbon
DMSP conversion to DMS	absolute rate of DMS increase in $CHCl_3$ incubations	75	possible overestimate due to $CHCl_3$ enhanced DMS production
Other DMSP losses	difference between DMSP turnover and conversion to DMS	155	
Biological DMS consumption	incubations with and without $CHCl_3$	50	possible overestimate due to $CHCl_3$ enhanced DMS production
DMS flux to atmosphere	DMS surface seawater concentration and wind speed	0.8	factor of 2 uncertainty due to transfer velocity wind speed relationship

* See text for details.

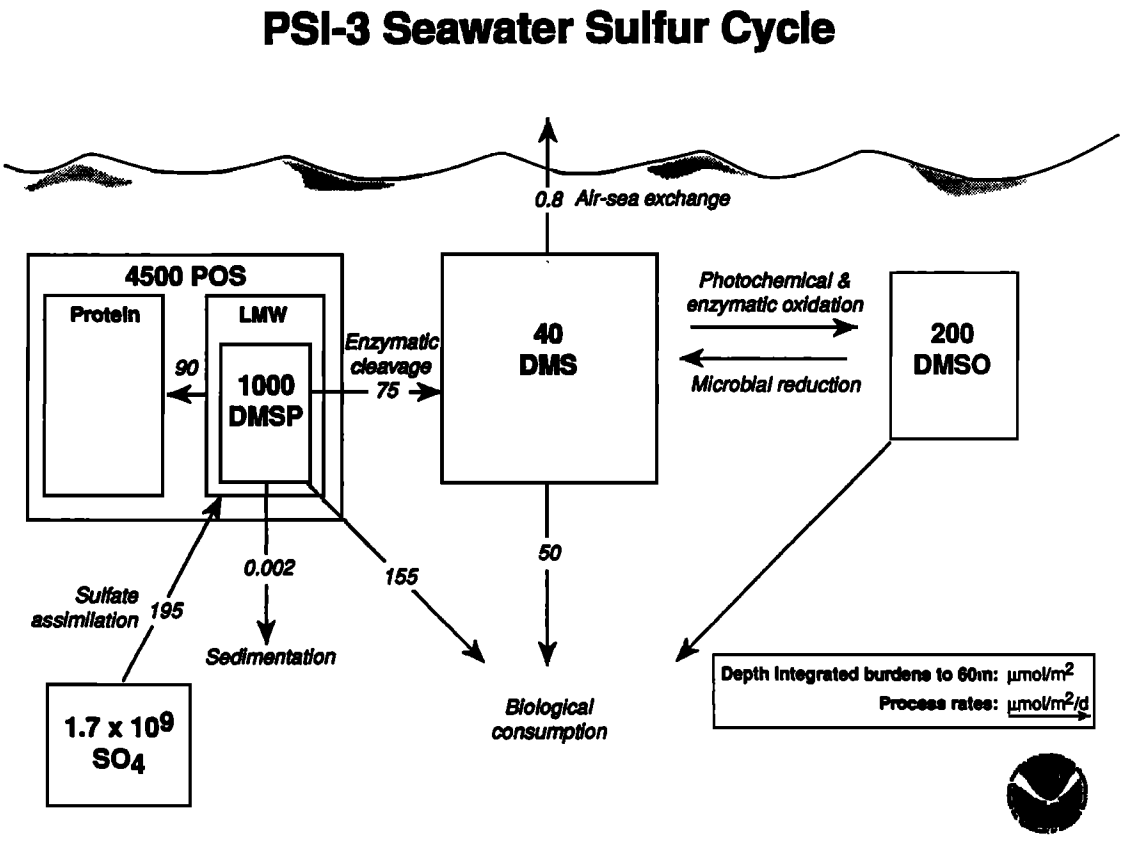

Figure 3. The seawater sulfur cycle at the time series station during PSI-3. The concentrations are average depth-integrated burdens (60 m) in µmoles/m^2. The processes affecting these burdens are in µmoles/m^2/d. Although the cycle does not always balance (i.e., DMSP consumption is higher than DMSP production), the burdens and rates represent the best estimates from the available measurements.

surface water column [*Taylor and Kiene*, 1989]. DMS can be lost from surface seawater by several mechanisms. Since atmospheric DMS concentrations are relatively low, there is a constant flux of seawater DMS to the atmosphere which is primarily controlled by surface turbulence and the liquid-phase DMS concentration [*Liss and Merlivat*, 1986; *Bates et al.*, 1987, 1992]. The average flux of DMS to the atmosphere during PSI-3 was 0.8 µmoles/m^2/d. DMS is also photooxidized in surface seawater, presumably to DMSO, at rates similar to losses by air-sea exchange [*Brimblecombe and Shooter*, 1986]. Although we have no measurements of the rate of DMSO formation, the average seawater DMSO burden during PSI-3 was 5 times higher than the DMS burden. The major loss of DMS from surface ocean waters appears to be through microbial consumption with DMS turnover times of the order of days [*Kiene and Bates*, 1990; *Leck et al.*, 1990; *Kiene and Service*, 1991]. The depth-integrated microbial consumption rates are generally more than 10 times higher than the loss of DMS to the atmosphere through air-sea exchange [*Wakeham et al.*, 1987; *Kiene and Bates*, 1990]. During PSI-3, most (⅔) of the DMS was consumed microbially with air-sea exchange accounting for only 1% of the DMS loss. Since DMS was confined to the upper photic zone with significant concentration gradients within the surface ocean mixed layer, losses due to vertical mixing were relatively insignificant. Based on the average depth-integrated burden of DMS and the average DMS production rate, the residence time of surface seawater DMS was only 13 hours.

Conclusions

Understanding the factors that control the concentration of DMS in surface waters, and ultimately its flux to the atmosphere, requires detailed knowledge of the sulfur cycle in surface seawater. The measurements from PSI-3 represent the most complete picture of this cycle to date and allow several major conclusions to be drawn with respect to DMS and its precursor DMSP. DMSP can be a major fraction (22%) of the total burden of reduced organic sulfur. However, high concentrations of DMSP do not necessarily imply high concentrations of DMS. The data from PSI-3 support the hypothesis that a large fraction of the total DMSP (67%) can cycle through other pathways [*Belviso et al.*, 1990; *Kiene and Service*, 1991]. The low DMS concentrations are also a result of relatively rapid biological consumption which during PSI-3 accounted for 67% of the total DMS consumption. As observed previously [*Kiene and Bates*, 1990], air-sea exchange accounted for only a small fraction of the DMS loss.

The integrated measurements described here are the first of their kind and provide us with a fairly detailed picture of the surface ocean sulfur cycle during PSI-3 (Figure 3). However, there are still many areas where our knowledge is incomplete and many questions remain. In a general sense, we still have a very poor understanding of the factors which control the production of DMSP by phytoplankton, the branching ratio in the degradation of DMSP, and the relative rates of biological and photochemical loss terms for DMS. The data presented

here are from one temperate latitude site characterized by high DMSP and low DMS concentrations. We do not know how this cycle will differ in other seasons and regions. In addition, we cannot predict how the seawater sulfur cycle would respond to a perturbation in climate. The concentration of DMS in surface seawater was certainly not limited by sulfate assimilation or DMSP production during PSI-3 which implies that minor changes in either the DMS production or consumption terms could have major effects on the seawater concentration of DMS and hence the air-sea exchange of DMS. The potential climatic importance of oceanic DMS emissions therefore requires a much better understanding of this seawater sulfur cycle.

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