

Regional and Seasonal Variations in the Flux of Oceanic Dimethylsulfide to the Atmosphere

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Dimethylsulfide (DMS) concentrations have been measured in over 1000 Pacific surface seawater samples during the past 4 years. The data have been tabulated to take into account both regional and seasonal variations in concentration. The area-weighted summer and winter concentrations of DMS in the North Pacific Ocean are 2.2 and 1.3 nmol/L, respectively. Wind speed, surface seawater temperature, and DMS diffusivities are used to calculate air-sea exchange coefficients. The area-weighted summer and winter DMS piston velocities are 2.3 and 2.7 m/d, respectively. These exchange coefficients combined with the concentration data yield a net ocean to atmosphere DMS flux in the North Pacific Ocean of 0.12 Tmol/yr. Extrapolating this calculation by regional areas to the global ocean yields a net DMS flux of 0.50 Tmol/yr, less than earlier estimates of 1.2 Tmol/yr, but still consistent with excess sulfate deposition estimates and model studies of the marine atmospheric sulfur budget. The uncertainty in the flux estimate is roughly a factor of 2.

INTRODUCTION

The surface ocean plays an important role in the global biogeochemical sulfur cycle. Gaseous sulfur compounds emitted from the ocean are a major source of sulfate aerosol in the marine troposphere [Bonsang *et al.*, 1980]. This aerosol is the major contributor to the acidity of natural precipitation [Charlson and Rodhe, 1982] and to cloud condensation nuclei and hence may be important to the radiative equilibrium of the earth [Shaw, 1983, and R. J. Charlson *et al.*, Atmospheric sulfur: Geophysiology and climate, submitted to *Nature*, 1986].

Observational studies to date have shown that dimethylsulfide (DMS) is the dominant volatile sulfur compound present in marine surface waters [Barnard *et al.*, 1982; Andreae and Raemdonck, 1983; Cline and Bates, 1983]. This compound accounts for greater than 95% of the observed reduced sulfur in surface ocean waters [Cline and Bates, 1983] and is therefore thought to be the only significant source of gaseous sulfur to the marine troposphere [Nguyen *et al.*, 1983; Andreae, 1986].

Lovelock *et al.* [1972] were the first to describe a marine source of DMS, which has been subsequently verified by several investigators [Barnard *et al.*, 1982; Andreae and Raemdonck, 1983; Cline and Bates, 1983]. The precursor of DMS (dimethylsulfoniopropionate, or DMSP) is produced by phytoplankton. DMS is both excreted by phytoplankton and released during zooplankton grazing [Dacey and Wakeham, 1986]. In support of its biological origin, DMS is normally restricted to the upper 200 m of the water column with maximum concentrations near the bottom of the mixed layer [Cline and Bates, 1983; Andreae and Barnard, 1984]. Below this maximum, the concentration decreases exponentially with depth to near-zero concentrations (<10 pmol/L) at 200 m. The surface layers are always observed to be supersaturated with DMS, implying a net flux to the atmosphere [Barnard *et*

al., 1982; Andreae and Raemdonck, 1983]. Once released to the atmosphere, the steady state concentration of DMS is kept quite low by rapid reaction with hydroxyl radicals [Graedel, 1979; Andreae *et al.*, 1985].

Early atmospheric sulfur budgets required the oceans be a net source of reduced sulfur. Model estimates ranged from 9 Tmol/yr [Eriksson, 1963] to 1 Tmol/yr [Granat *et al.*, 1976] and were based solely on the amount of additional sulfur needed to balance the global budget. The most recent estimate, based on observations in the Atlantic and eastern tropical Pacific, suggests a value near 1 Tmol/yr [Andreae and Raemdonck, 1983; Galloway, 1985; Andreae, 1986]. All current estimates of the marine DMS flux suffer from relatively poor definition of the seasonal mean DMS concentrations. In particular, there are almost no winter measurements of DMS from any portion of the world oceans.

In this report, we discuss our observations taken in the Pacific Ocean during the past 4 years (Figure 1). These observations include three meridional sections, two zonal sections along the equator, and one across the North Pacific at mid-latitude. Several transects were repeated to assess the seasonal dependence on DMS concentrations. One cruise in the South Pacific Ocean (April 1984) provides a limited data set for comparison with the North Pacific data. These concentration data are used to compute revised flux estimates of DMS to the atmosphere. This is the first oceanic sulfur flux estimate to take into account area-weighted, seasonal DMS concentrations.

METHODS

Water samples were collected using either 5-L Niskin bottles, the ship's biological pumping system (bow intake at approximately 5-m depth), the ship's sea chest (midship intake at approximately 5-m depth), or a polyvinyl chloride bucket. Experiments conducted to compare the various sampling methods showed no significant differences in DMS concentrations between methods when sampling the same parcel of water. Aliquots of these samples (15-30 mL) were transferred to a 50-mL aqueous gas stripper and purged with ultrapure hydrogen at 60 mL/min. Gas transfer lines were made of fused-silica capillary (1982-1983) or teflon tubing (1984-1985) for chemical inertness and to reduce dead volume. All glassware

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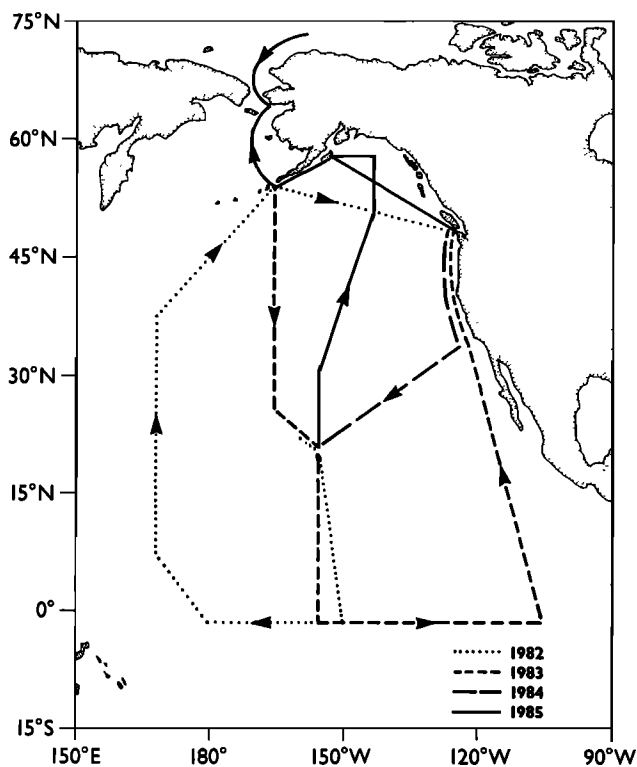


Fig. 1. Cruise tracks along which reduced sulfur compounds were measured during 1982–1985.

was deactivated with functional silane [Farwell and Gluck, 1980] to minimize sulfur adsorption on surfaces. Water vapor was selectively removed from the stripper gas stream in a cold finger held at -30°C , while the sulfur gases were trapped on either a silanized glass-bead trap (1982–1984) held at liquid nitrogen temperature or on a teflon trap (1985) held at liquid argon temperature. After purging the water sample (15–30 min, depending on volume), the sulfur cold trap was quickly heated and the volatile compounds transferred to a fused silica loop in liquid nitrogen for preconcentration at the head of the column before chromatographic separation (Hewlett-Packard model 5730 GC) on a DB-5 thick film ($1\ \mu\text{m}$) (1982–1983) (J & W Scientific, Cordova, California) or a 5% methyl silicon thick film ($5\ \mu\text{m}$) (1984–1985) (Perkin Elmer, Norwalk, Connecticut) fused silica column. Sulfur compounds were detected with a flame photometric detector, the response of which was calibrated against Metronics certified permeation tube standards (Dynacal Metronics Inc., Santa Clara, California). These certified standards have been intercompared with S. Hoyt and R. Rasmussen of the Oregon Graduate Center and with Airco certified gas standards and found to be within the stated 10% accuracy. Precision for the analysis of DMS is typically $\pm 10\%$ (1 standard deviation expressed as a percentage of the mean), based on replicate analysis of a single water sample. Identification of the volatile sulfur compounds was made on the basis of retention time and confirmed by gas chromatographic/mass spectrometric analysis (Hewlett-Packard model 5992 gas chromatograph/mass spectrometer) on selected samples.

The performance of the analytical system was monitored by regularly running sulfur standards and blanks through the entire system. Recovery of DMS from seawater was generally $>90\%$ and blank values $<2\ \text{pmol}$ (0.2% of a typical surface

sample). The tabulated values reported here are blank and recovery corrected.

RESULTS

Equatorial Pacific

Measurements of DMS and relevant water properties were made westward from 148°W along the equator in May 1982 and eastward from 158°W in April 1983. Vertical profiles were taken at selected locations with near-surface samples collected en route between locations. Surface distributions of DMS along the equator are shown in Figure 2 and Table 1.

There appears to be little zonal gradient in the concentration of DMS between 148°W and 180°W (May 1982), but farther west, concentrations decreased significantly (Figure 2), presumably the result of decreased primary production in the western Pacific [Cline and Bates, 1983]. Assuming that spatial variations are largely due to the patchiness of phytoplankton and to local variations in the degree of vertical mixing, the average DMS concentration between 148°W and 180°W was $3.8 \pm 1.1\ \text{nmol/L}$ ($n = 41$), decreasing to $1.9 \pm 0.5\ \text{nmol/L}$ ($n = 17$) west of 180°W (Table 1).

The following year, 1983, DMS measurements in the central and eastern equatorial Pacific (Figure 2) coincided with the mature phase of the major equatorial surface warming of the 1982–1983 El Niño Southern Oscillation (ENSO) event [Rasmusson and Wallace, 1983]. The southeast trades had been replaced by weak westerlies, which reduced the intensity of equatorial upwelling, as evidenced by positive sea surface temperature anomalies of approximately 2°C [Cane, 1983]. Even so, concentrations of DMS along the equator remained relatively high and averaged $2.7 \pm 0.8\ \text{nmol/L}$ ($n = 160$) (Table 1). Large spatial variability was observed, similar to that reported by Andreae and Raemdonck [1983] for the previous year. Comparing our measurements made in April 1983 with those of Andreae and Raemdonck taken in June 1982, there appears to have been little change in the average concentration of DMS west of 105°W (Figure 1; Andreae and Raemdonck [1983]). Similarly, our chlorophyll *a* concentrations between 105°W and 158°W were $56 \pm 12\ \text{ng/L}$, nearly identical to that reported by Andreae and Raemdonck. Apparently, the ENSO event had little effect on the concentrations of chlorophyll *a* or DMS in this region. In the zone of stronger upwelling to the east, Barber and Chavez [1983] have shown the standing stock of phytoplankton (chlorophyll *a*) changed very little during the 1982–1983 ENSO event at 95°W ; however, the biological activity of these plankton (primary productivity) decreased by

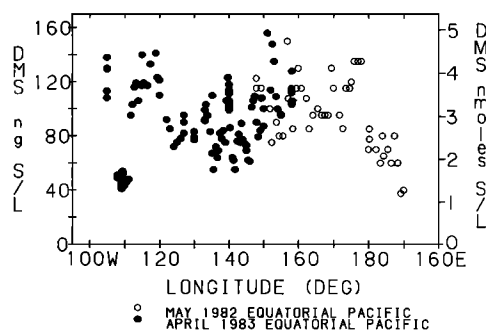


Fig. 2. Surface concentrations of DMS in the eastern and central equatorial Pacific. Measurements in April 1983 coincided with the equatorial El Niño event, which began the previous fall.

TABLE 1. Surface Seawater DMS Concentrations in the Pacific Ocean (1982–1985)

Location	Date	Count	Median	Mean	Standard Deviation	Minimum	Maximum
32°–49°N, U.S. coast	May 1983	135	1.28	1.44	0.66	0.53	4.06
	Feb. 1984	24	0.56	0.66	0.19	0.41	1.28
	Sept. 1984	84	1.97	2.50	2.16	0.31	11.88
	May 1985	108	2.34	2.84	2.00	0.44	11.56
32°–49°N, Estuaries	Sept. 1984	55	3.13	5.31	5.94	0.91	34.38
65°–73°N, Alaska coast	Sept. 1985	107	1.38	1.53	0.84	0.34	4.00
50°–65°N Alaska coast	June 1982	14	2.81	3.44	3.44	1.09	14.06
	July 1985	42	5.00	12.19	20.31	1.38	90.63
	Sept. 1985	38	3.75	5.94	5.31	0.47	19.69
35°–50°N, 165°E	June 1982	2	2.03	2.03	0.00	2.03	2.03
35°–50°N, 170°W	March 1983	16	0.66	0.78	0.25	0.47	1.31
35°–50°N, 145°–152°W	July 1985	13	2.25	2.56	0.75	1.34	3.75
20°–35°N, 165°E	June 1982	3	1.25	1.25	0.16	1.09	1.41
20°–35°N, 170°W	March 1983	8	0.91	0.94	0.38	0.53	1.44
20°–35°N, 130°–158°W	Feb. 1984	25	0.66	0.69	0.13	0.50	1.06
20°–35°N, 152°–155°W	July 1985	17	2.31	2.16	0.78	1.00	3.44
5°–20°N, 155°W	May 1982	13	1.41	1.72	0.78	1.25	3.75
5°–20°N, 158°–170°W	April 1983	25	2.19	2.16	0.94	0.94	4.69
5°–20°N, 105°W	April 1983	24	1.41	1.47	0.25	1.06	2.06
0°–5°N, 148°–180°W	May 1982	41	3.75	3.75	1.13	2.34	6.88
0°–5°N, 180°–168°E	May 1982	17	1.88	1.88	0.50	1.19	2.66
0°–5°N, 105°–158°W	April 1983	160	2.59	2.66	0.81	1.28	5.00
0°–5°N, 170°W	April 1984	7	2.94	2.97	0.63	1.78	4.06
0°–5°S, 105°–158°W	April 1983	59	3.75	3.44	0.91	1.53	5.00
0°–5°S, 170°W	April 1984	10	3.75	3.75	0.94	1.19	4.69
5°–20°S, 170°W	April 1984	13	1.06	1.09	0.13	0.91	1.38
20°–35°S, 170°W	April 1984	7	1.00	1.06	0.13	0.84	1.22
35°–55°S, 150°–170°W	April 1984	23	2.00	2.75	1.72	1.22	6.25

Total number of samples is 1090. DMS concentrations are expressed in nanomoles of sulfur per liter.

fivefold during the mature phase of the ENSO. Although there was little taxonomic change during the ENSO, there were fewer diatoms and more microflagellates during the peak of the anomaly [Barber and Chavez, 1983]. This could have potentially affected DMS production, which has been shown to be species specific [Barnard et al., 1984].

Meridional Distributions

Surface distributions of DMS along two meridional transects in the North Pacific in March–April 1983 are summarized in Figure 3. Large spatial variations in the concentration of DMS were observed south of 10°N along 158°W. Concentrations ranged from 1.5 to 5.0 nmol/L. North of 14°N, the concentration of DMS was quite uniform, ranging from 0.5 to 1.5 nmol/L. The mean concentration north of 20°N was only 0.9 ± 0.4 nmol/L. In contrast, the mean concentration in this region during July 1985 was 2.3 ± 0.8 nmol/L (Table 1). In the eastern tropical North Pacific (Figure 3), surface concentrations in April 1983 ranged from 1.4 to 5.0 nmol/L, with a maximum observed near 2°S. In a normal year, we believe this maximum would have occurred along or slightly north of the equator [Andreae and Raemdonck, 1983; Cline and Bates, 1983]; however, the unusual meteorological conditions during the ENSO event caused a southward displacement in the Intertropical Convergence Zone, the southeast trade winds, and equatorial upwelling. The high DMS concentrations at 2°S could correspond to the divergence between the westward flowing south equatorial current and the eastward flowing equatorial countercurrent (ECC). Both currents were displaced southward during the ENSO such that the ECC was actually on the equator at this longitude as evidenced by the easterly current.

The seasonal distributions of DMS along the west coast of

the United States have been discussed in a previous paper [Bates and Cline, 1985]. In summary, concentrations vary by a factor of 3 between summer and winter, with mean concentrations of 1.8 and 0.6 nmol/L, respectively. The data for the four coastal cruises (May 1983 to May 1985) are summarized in Table 1. Also summarized in Table 1 are concentration data for the major estuaries along the west coast of the United States. Estuarine DMS concentrations ranged from 1.9–34 nmol/L with a median concentration of 3.1 nmol/L.

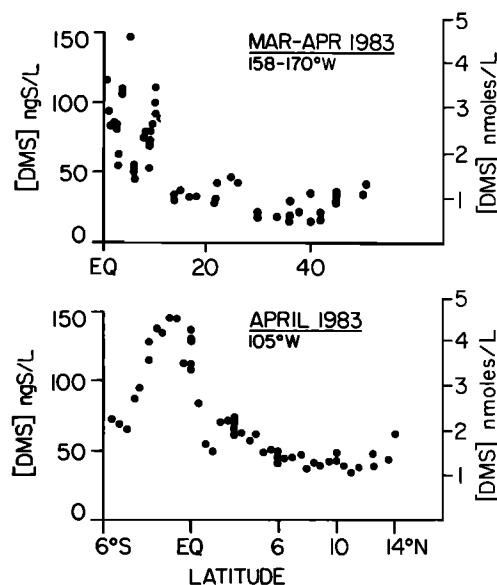


Fig. 3. Surface concentrations of DMS in the central and eastern North Pacific in spring 1983.

TABLE 2. Surface Seawater DMS Concentrations From the Literature

Region	Reference*	Date	Count	Mean	Minimum	Maximum
Coastal	1	Nov. 1981			0.03	3.13
Florida	2	May 1983		0.44		
England	2	June 1983		15.63		
Peru	3	June 1982		6.88	0.94	43.75
Subarctic, Bering Sea	4	May 1981		4.69	1.00	17.06
South Pacific, 17°–36°S	5	Nov. 1982	12	4.38	2.19	6.56
Pacific						
80°–140°W, 0°–5°N	6	July 1982		3.13		
140°W, 5°–20°N	6	July 1982		1.88		
Sargasso Sea, 25°N	7	Sept. 1981		2.22	0.94	4.06
Atlantic, 53°N–36°S	7	Oct. 1980	231	2.84	0.56	23.13

DMS concentrations are expressed in nanomoles of sulfur per liter.

*1, *Froelich et al.* [1985]; 2, *Turner and Liss* [1985]; 3, *Andreae* [1985]; 4, *Barnard et al.* [1984]; 5, *Nguyen et al.* [1984]; 6, *Andreae and Raemdonck* [1983]; and 7, *Andreae and Barnard* [1984] (the average concentration given here for the Atlantic Ocean is biased by high concentrations in the Rio De La Plata estuary. The average concentration for the open Atlantic Ocean surface waters based on the data from this *Meteor* cruise is 1.9 nmol of sulfur per liter [*Andreae et al.*, 1983]).

Measured DMS concentrations in the Gulf of Alaska, Bering, Chukchi, and Beaufort seas are also quite variable. Although part of this area is ice covered for much of the year, the median concentration during the summer months ranged from 1.4 to 5.0 nmol/L (Table 1). Similar high concentrations were observed by *Barnard et al.* [1984].

One cruise was conducted to the South Pacific Ocean in March–April 1984. Although the data set is quite limited, the measured DMS concentrations are similar to values obtained in comparable latitudes and seasons in the North Pacific (Table 1).

DISCUSSION

DMS Concentrations

Interest in the ocean's role in regional and global atmospheric sulfur cycles has prompted numerous studies to determine DMS concentrations in both the surface ocean and the atmosphere. The surface seawater DMS data available in the literature (Table 2) agree quite well with our data (Table 1). The reported mean concentration of DMS in the Bering Sea in June 1982 is 4.7 nmol/L [*Barnard et al.*, 1984], as compared with a median concentration in the Gulf of Alaska in July 1985 of 5.0 nmol/L. The mean concentration of DMS near the equator from 80° to 140°W in July 1982 was 3.1 nmol/L [*Andreae and Raemdonck*, 1983], as compared with our median eastern equatorial concentration of 2.8 nmol/L. The DMS concentration in the tropical (5°–20°N) Pacific along 140°W in July 1982 averaged 1.9 nmol/L [*Andreae and Raemdonck*, 1983] compared with our median tropical DMS concentration of 1.7 nmol/L. The data from the Atlantic Ocean also compare well with our Pacific Ocean data. The mean concentration of DMS in the Sargasso Sea (25°N) in September 1981 was 2.2 nmol/L [*Andreae and Barnard*, 1984] as compared with our median subtropical region (20°–35°N) summer concentration of 2.2 nmol/L. The mean concentration of DMS in the non-coastal Atlantic Ocean in October 1980 was 1.9 nmol/L [*Andreae et al.*, 1983], which is equal to our area-weighted annual mean DMS concentration in the North Pacific Ocean.

DMS concentrations in coastal waters are quite variable. In both tropical estuaries (Rio De La Plata, *Andreae and Barnard* [1984]) and upwelling areas (Peru, *Andreae* [1985]) the average concentrations are high (mean concentration in June

1982 off Peru of 6.9 nmol/L [*Andreae*, 1985]). However, in temperate coastal waters the concentrations are very seasonally dependent. *Turner and Liss* [1985] found a 35-fold change in concentration between May and June along the English coast. The average seasonal difference in concentration along the west coast of the United States is a factor of 3 [*Bates and Cline*, 1985]. Although median DMS concentrations in the coastal ocean are harder to define, liberally defining the coastal ocean as the area with water depths less than 400 m, the coastal ocean makes up only 6% of the total ocean area [*Levitus*, 1982] and therefore has little effect on a global DMS flux.

The seasonal dependence of DMS concentrations is graphically shown in Figure 4, where the literature DMS values (Table 2), are combined with the data from this study. Southern hemisphere values are offset by 6 months, and a curve has

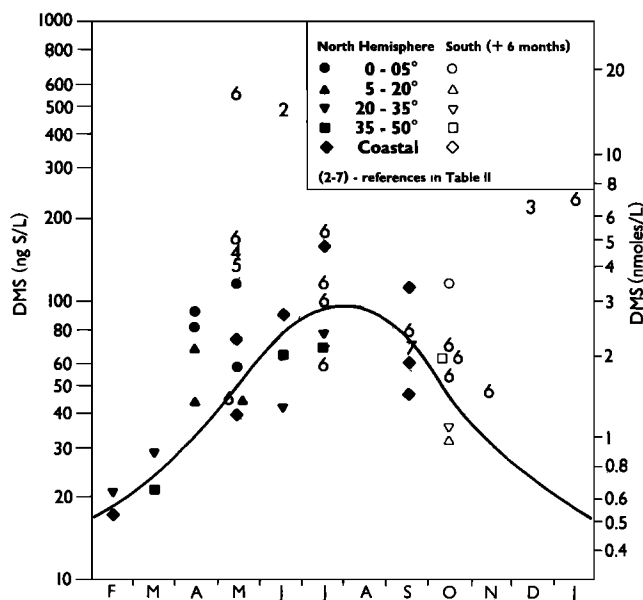


Fig. 4. The seasonality of oceanic DMS concentrations. The southern hemisphere values have been offset by 6 months. The numbers refer to literature DMS values referenced in Table 2. The symbols refer to the data from Table 1. The line intersects the means of the subtropical, temperate, and coastal values.

TABLE 3. Regional Physical and Meteorological Data Used to Compute DMS Diffusivities and Exchange Coefficients

Region	Winter			DMS Diffusivity, $\times 10^{-5}$ cm ² /s	Summer			DMS Diffusivity $\times 10^{-5}$ cm ² /s
	Wind Speed, m/s	Water Temperature, °C	Water Viscosity, cP		Wind Speed, m/s	Water Temperature, °C	Water Viscosity, cP	
Arctic, 65°–80°N	6.3	ice		0.00	6.9	4	1.65	0.59
Subarctic, 50°–65°N	8.8	2	1.76	0.55	6.9	5	1.60	0.61
Temperate, 35°–50°N	9.9	11	1.35	0.74	7.1	15	1.21	0.84
Subtropical, 20°–35°N	7.7	21	1.05	0.99	6.5	24	0.98	1.07
Tropical, 5°–20°N	6.8	26	0.93	1.14	6.5	27	0.91	1.17
Equatorial, 0°–5°N	5.5	27	0.91	1.17	5.3	27	0.91	1.17

Winter is November to April, summer is May to October, and arctic summer is July to October. Wind speed and water temperature are from the Marine Climatic Atlas of the World [U.S. Govt. Printing Office, 1977]. Seawater (35 ppt) viscosities are from Riley and Skirrow [1975]. DMS diffusivity is calculated from Wilke and Chang [1955], updated using Hayduk and Laudie [1974].

been drawn to intersect the means of the subtropical, temperate, and coastal values. The equatorial values show little seasonal dependence, while the higher latitude DMS concentrations vary seasonally by approximately a factor of 4. The atmospheric oxidation products of DMS (methanesulfonic acid (MSA) and sulfate) show a similar seasonal trend [Saltzman *et al.*, 1986]. The average atmospheric concentrations of MSA and non-sea-salt sulfate are fairly constant in the tropics ($\pm 20\%$ at Fanning and American Samoa), while average concentrations in the subtropics and temperate regions (Shemya, Midway, New Caledonia, and Norfolk) vary seasonally by a factor of 2–12 [Saltzman *et al.*, 1986]. MSA also shows a distinct seasonal trend in the temperate South Pacific Ocean, varying by roughly a factor of 10 [Ayers *et al.*, 1986]. There is ample evidence therefore for the seasonality of DMS concentrations in the ocean and its oxidation products in the atmosphere.

Sea to Air Transfer

The primary interest in oceanic DMS is its impact on atmospheric sulfur cycles. In recent years, DMS flux estimates have been made on regional [Cline and Bates, 1983; Bates and Cline, 1985], oceanic [Barnard *et al.*, 1982], and global scales [Andreae and Raemdonck, 1983]. The major difficulty in making globally representative annual DMS flux estimates is

in reliably averaging over the large seasonal and spatial variability in measured DMS concentrations. The lack of winter data has seriously biased past global estimates. In order to quantify the flux of DMS to the atmosphere, taking into account seasonal and spatial variability, we have divided the year into summer and winter seasons, and the North Pacific Ocean into nine regions. The midpoints of the seasons (winter (November to April) and summer (May to October)) are offset from the solstices by 2 months to account for the lag in ocean warming. The extraequatorial region is divided by latitude into five zones (Table 3). The equatorial region is divided longitudinally at 180°W because of the zonal concentration gradient, with higher DMS concentrations in the eastern zone of stronger upwelling. The coastal ocean is defined as the area with water depths less than 400 m and is broken into two regions (0°–20°N and 20°–50°N).

The flux of DMS across the air-sea interface is usually estimated from gas exchange models [Liss, 1973], which predict that the flux is proportional to the product of the concentration difference across the air-sea interface and a first-order exchange coefficient ($V(p)$) such that the flux equals $V(p)\{[\text{DMS}] - b[\text{DMS}_{\text{air}}]\}$, where $b[\text{DMS}_{\text{air}}]$ is the equilibrium solubility concentration (b is the Bunsen coefficient, and $[\text{DMS}_{\text{air}}]$ is the atmospheric partial pressure) and $[\text{DMS}]$ is the observed DMS concentration in the mixed layer. It is

TABLE 4. Regional Exchange Coefficients Calculated From Wind Data in Table 3

Region	Location, deg North	Winter			Summer			Winter DMS	Summer DMS
		Radon* $m = 0.66$ $b = 3$	Radon† $m = 0.46$ $b = 2.7$	Radon‡ $m = 1.0$ $b = 3.6$	Radon* $m = 0.66$ $b = 3$	Radon† $m = 0.46$ $b = 2.7$	Radon‡ $m = 1.0$ $b = 3.6$		
Arctic	65–80				2.57	1.93	3.3		1.53
Subarctic	50–65	3.83	2.81	5.2	2.57	1.93	3.3	2.12	1.58
Temperate	35–50	4.55	3.31	6.3	2.71	2.02	3.5	3.35	2.24
Subtropical	20–35	3.10	2.30	4.1	2.31	1.75	2.9	2.98	2.39
Tropical	5–20	2.51	1.89	3.2	2.31	1.75	2.9	2.75	2.59
Equatorial	0–5	1.65	1.29	1.9	1.52	1.20	1.7	1.85	1.50

The data have been adjusted for 20°C and a 20-m wind height [see Smethie *et al.*, 1985]. The exchange coefficients (V_p) are calculated assuming $V_p = m(\text{wind speed}) - b$. DMS exchange coefficients are based on temperature and diffusivity data from Table 3 and radon exchange coefficients from Smethie *et al.* [1985]. Corrections were made assuming exchange coefficients vary with the square root of the molecular diffusivity divided by the viscosity [$V_p(\text{DMS}) = V_p\{\text{Diff}(\text{DMS})/\text{Viscos}(\text{DMS})\}^{0.5}/(1.14 \times 10^{-5} \text{ cm}^2/\text{s}/1.12 \text{ cp})^{0.5}$]. Winter is November to April, and summer is May to October. Exchange coefficients are expressed in meters per day.

*Smethie *et al.* [1985].

†Wanninkhof *et al.* [1985].

‡Broecker *et al.* [1978].

TABLE 5. North Pacific DMS Fluxes

Region	Area, 10 ¹² m ²	Winter			Summer			Annual Flux, Gmol S/yr
		Concen- tration, nmol S/L	V _p , m/d	Flux, μmol S/m ² /d	Concen- tration, nmol S/L	V _p , m/d	Flux, μmol S/m ² /d	
Arctic, 65°–80°N	2	0		0.00	1.38	1.53	2.11	0.5
Subarctic, 50°–65°N	6	0.66	2.12	1.40	4.16	1.58	6.57	8.7
Temperate, 35°–50°N	13	0.66	3.35	2.21	2.22	2.24	4.96	17.0
Subtropical, 20°–35°N	20	0.72	2.98	2.15	2.15	2.39	5.14	26.6
Tropical, 5°–20°N	28	1.72	2.75	4.72	1.72	2.59	4.45	46.9
Equatorial								
80°–180°W, 0°–5°N	6.1	2.83	1.85	5.24	2.83	1.70	4.82	11.2
180°–120°E, 0°–5°N	3.7	1.88	1.85	3.48	1.88	1.70	3.20	4.5
Coastal, <400 m								
20°–50°N	1.4	0.56	3.17	1.77	1.83	2.31	4.23	1.5
0°–20°N*	1.6	5.00	2.52	12.61	5.00	2.37	11.84	7.1
Total, 0°–65°N	82							120
Area Weighted average		1.35	2.74	3.50	2.25	2.28	4.97	

Areas are from *Levitus* [1982]. DMS concentrations are from Table 1. DMS exchange coefficients (V_p) are from Table 4. Winter is November to April, and summer is May to October.

*Data from *Andreae and Raemdonck* [1983].

easily shown that the equilibrium solubility concentration is quite small relative to the observed surface water DMS values [*Cline and Bates*, 1983; *Barnard et al.*, 1982]; hence flux $DMS = V(p)[DMS]$.

While the measurement of the surface concentration of DMS is straightforward, calculating a reliable value of the exchange coefficient, $V(p)$, is more difficult. For the range of wind speeds encountered, it is generally accepted that $V(p)$ is linearly proportional to the wind speed ($V(p) = m(\text{wind speed}) - b$) with threshold velocities (b) ranging from 2.7 to 3.6 m/s at a 20-m height and slopes (m) ranging from 0.46 to 1.0 (Table 4). The lower threshold and slope are based on a lake study [*Wanninkhof et al.*, 1985], while the higher threshold and slope are from wind tunnel experiments [*Broecker et al.*, 1978]. *Smethie et al.* [1985], using radon measurements in the Atlantic Ocean, obtained a threshold and slope intermediate between the two earlier studies. The exchange coefficient is also a function of molecular diffusivity and has been shown to vary with the square root of the diffusivity [*Holmen and Liss*, 1984; *Ledwell*, 1984]. The molecular diffusivity for DMS can be calculated from the water temperature and viscosity [*Hayduk and Laudie*, 1974]. The mean seasonal wind speed, water temperature, water viscosity, and DMS diffusivity are given for each region in Table 3, and the radon exchange coefficients calculated from wind speeds are shown in Table 4. The winter and summer DMS exchange coefficients for each region are computed in Table 4 based on the temperature and diffusivity data from Table 3 and the wind relationship of *Smethie et al.* [1985].

These exchange coefficients are then combined with regional concentration data from Table 1 and regional areas [*Levitus*, 1982] to compute seasonal DMS fluxes (Table 5). We assume the concentration of DMS does not vary seasonally in the tropical and equatorial regions. The summer tropical DMS concentrations (July 1982) of *Andreae and Raemdonck* [1983] are nearly identical to our winter values. We have also adopted the tropical coastal DMS concentrations of *Andreae and Raemdonck* [1983]. The results of these calculations for the North Pacific Ocean show an area-weighted, mean DMS

concentration of 1.3 nmol/L in the winter and 2.2 nmol/L in the summer. The area-weighted mean exchange coefficients are 2.7 m/d in the winter and 2.3 m/d in the summer. The total annual flux of DMS from the North Pacific Ocean is 0.12 Tmol/yr. Extrapolating these data regionally to the global ocean gives a total flux of 0.50 Tmol/yr (Table 6).

There are several sources of uncertainty in this global flux estimate. Although the concentration data are based on over 1000 samples and agree well with other studies, the mean standard deviation for the seasonal concentration in each region is ~30% (calculated from Table 1). We have arbitrarily defined the seasons to be of equal length and have neglected interannual variability. There are very limited data from the southern oceans, where the productive regions and high winds near Antarctica may appreciably influence the global flux. The exchange coefficients based on *Smethie et al.* [1985] appear to be intermediate between the lake and wind tunnel results. The range of potential values adds another ~30% uncertainty (Table 4). The exchange coefficients must be adjusted for DMS based on diffusivity, which adds another ~10% uncertainty. The product of these uncertainties results in a factor of 2 uncertainty in the flux of DMS to the atmosphere.

COMPARISONS WITH OTHER STUDIES

Andreae and Raemdonck [1983] have used surface seawater DMS concentrations to calculate a global flux of 1.2 Tmol/yr from the ocean to the atmosphere. As previously discussed (Table 2), our concentration data agree quite well with each other. Our calculations also use similar exchange coefficients. *Andreae and Raemdonck* used a global average exchange coefficient of 2.8 m/d. Our area-weighted mean summer and winter exchange coefficients are 2.3 and 2.7 m/d, respectively. The difference in exchange coefficients therefore accounts for only 10% of the difference in the DMS flux calculations. Although our concentration measurements and exchange coefficients are similar, *Andreae and Raemdonck* calculate much higher regional emission rates (Table 6). The difference between our estimates and those of *Andreae and Raemdonck* lies largely in the way in which they calculated the regional

TABLE 6. Global Oceanic DMS Fluxes

Region	North Pacific,* 10 ¹² m ²	Total World Ocean, 10 ¹² m ²	Sulfur Flux, Gmol S/yr		Emission Rate, mmol S (DMS)/m ² /yr		
			North Pacific†	Total Global‡	This Study	<i>Andreae and Raemdonck</i> [1983]	Area Total,§ 10 ¹² m ²
Arctic, 65°–80°	2	19	0.5	4.8	0.26		
Subarctic, 50°–65°	6	48	8.7	69.8	1.46	4.79	
Temperate, 35°–50°	13	67	17.0	87.7	1.31	2.13	83
Subtropical, 20°–35°	20	77	26.6	102.5	1.33		
Oligotrophic						2.14	148
Tropical, 5°–20°	28	92	46.9	154.1	1.68		
Equatorial 0°–5°	9.8	32	15.8	51.3	1.60	3.83	
Upwelling						5.65	86
Coastal, < 400 m							49
20°–50°	1.4	6	1.5	6.6	1.10	1.77	
0°–20°	1.6	6	7.1	26.8	4.46	4.35	
Total	82	347	120	500			366
Area weighted average					1.45	3.09	

*From *Levitus* [1982].

†Data from Table 5.

‡Extrapolated from the North Pacific flux.

§From *Andreae and Raemdonck* [1983].

mean concentrations of DMS. The large data base available today points out two problems with the earlier estimates. First, there is a strong seasonal dependence in DMS concentrations in extratropical surface waters (Figure 4). This was not adequately taken into account in the early flux estimates. Second, the Peru upwelling area and Rio de la Plata estuary are not representative of upwelling and coastal areas outside the tropics (coastal data in Tables 1 and 2). These areas were highly weighted in early estimates of the global flux, since a majority of the samples came from these regions. Together, these two factors bias the earlier estimates of the global DMS flux by at least a factor of 2 upward.

The flux of sulfur from the ocean to the atmosphere is only one part of the atmospheric sulfur cycle, and hence the flux of sulfur must balance the photochemical oxidation of DMS in the atmosphere and the deposition of sulfur from the atmosphere. The atmospheric chemistry of DMS has recently been summarized by *Andreae et al.* [1985], who reported average concentrations of DMS in the atmosphere, in the regions studied, of 2–3 nmol/m³. Constrained by estimated reaction rates of DMS in the atmosphere, this atmospheric DMS concentration supports the ocean-atmosphere flux of 1.2 Tmol/yr. However, all the atmospheric DMS measurements were made during the summer, when concentrations of DMS in the surface waters are high. Recent measurements (May 1985) of atmospheric DMS over the northeast Pacific Ocean at mid-latitudes have shown much lower DMS concentrations (0.25–1.25 nmol/m³, *Andreae et al.* [1987]). If we assume that the concentration of DMS in the atmosphere is proportional to the concentration in surface seawater, the flux of sulfur to the atmosphere necessary to balance the reaction rates would be cut by a factor of 2. Obviously, additional atmospheric DMS measurements are needed during the winter months to resolve this discrepancy.

The deposition of excess sulfate (non-sea-salt sulfate) over the remote Pacific Ocean (free of continental influence) has been estimated at 1.1 mmol/m²/yr [*Savoie*, 1984]. This com-

pares well with our emission rate in this area (1.3 mmol/m²/yr (Table 6)). *Kritz* [1982] examined a stationary boundary layer model that included the sea and the free troposphere as sources and sinks of sulfur. Balancing the steady state concentrations of SO₂ and excess sulfate, he concluded that the global marine flux of reduced sulfur compounds was about 0.46 Tmol/yr. The difficulty with this comparison is in the uncertain conversion efficiency of DMS to excess sulfate in the atmosphere. Although methane sulfonic acid (MSA) concentrations are only about 7% of the excess sulfate concentrations in the atmosphere [*Saltzman et al.*, 1983], laboratory studies suggest the conversion of DMS to MSA is much higher [*Hatakeyama et al.*, 1985; *Grosjean*, 1984; *Niki et al.*, 1983]. MSA, however, may in turn be a source of excess sulfate in the atmosphere [*Saltzman et al.*, 1983]. Therefore our flux of 0.5 Tmol/yr to the atmosphere is sufficient to account for the deposition of excess sulfate, assuming that intermediate oxidation products of DMS (e.g., MSA) are primarily converted to sulfate.

There are numerous other estimates of excess sulfate deposition [*Galloway*, 1985]. *Galloway and Gaudry* [1984] have shown a seasonality in the deposition of excess sulfate at Amsterdam Island that may reflect the seasonality in the DMS flux. Their calculated flux, however, is 2.7 mmol/m²/yr, a factor of 2 higher than our annual temperate region DMS flux. *Galloway* [1985] estimates the total non-sea-salt sulfur (e.g., wet and dry deposition of excess sulfate and dry deposition of sulfur dioxide) deposition over the oceans at 4.4 mmol/m²/yr. The difficulty in comparing sulfur deposition with DMS fluxes is that excess sulfate over the ocean is often impacted by continental sulfur sources [*Prospero et al.*, 1985]. Island measurements also have the potential interferences of local contamination [*Galloway and Gaudry*, 1984], biological productivity in the nearshore (surf zone) environment, and high rainfall amounts due to orographic effects [*Reed*, 1980]. What is needed to resolve the differences in DMS flux and excess sulfate deposition is a coordinated program of con-

current measurements of oceanic sulfur gases, and atmospheric sulfur gases and aerosols during conditions when there is no influence from continental air masses.

In summary, based on measurements in the North Pacific Ocean, the global marine source of DMS to the atmosphere is ~ 0.5 Tmol/yr (1.4 mmol/m²/yr) and is consistent with current observations and model studies, given the uncertainties in the air-sea exchange rate, oceanic and atmospheric DMS concentrations, and the kinetics of DMS oxidation in the marine boundary layer. The uncertainty in this calculated global marine DMS flux to the atmosphere is approximately a factor of 2.

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