Concentrations and Fluxes of Dissolved Biogenic Gases (DMS, CH₄, CO, CO₂) in the Equatorial Pacific During the SAGA 3 Experiment

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The equatorial Pacific Ocean is a source of both sulfur and carbon to the atmosphere. In February and March 1990, as part of the Soviet-American Gases and Aerosols (SAGA 3) expedition, dimethysulfide (DMS), methane (CH₄), carbon monoxide (CO), and carbon dioxide (CO₂) partial pressures were determined in both surface seawater and the overlying atmosphere of the central equatorial Pacific Ocean (15°N to 10°S, 145°W to 165°W). The partial pressures were used to calculate the net flux of these gases from the ocean to the atmosphere. The average regional DMS and CO fluxes were similar, 7.1 and 4.2 μmol/m²/d, respectively. The mixing ratio of CH₄ in surface seawater was close to equilibrium with the overlying atmosphere and hence the average flux was only 0.39 μmol/m²/d. The flux of CO₂ clearly dominated the air-sea carbon exchange with an average regional flux of 5.4 mmol/m²/d.

INTRODUCTION

Concentrations of carbon and sulfur gases are increasing in the troposphere as a result of anthropogenic emissions [Intergovernmental Panel on Climate Change (IPCC), 1990]. These gases affect the Earth's climate by absorbing the Earth's outgoing radiation (CO₂, CH₄), altering tropospheric photochemistry (CO, sulfur gases, hydrocarbons), or forming aerosol particles (sulfur gases). In order to assess the climatic effects of increasing anthropogenic emissions it is important to quantify the natural background emissions of the radiatively and photochemically important species.

DMS, CH₄, CO, CO₂, and nonmethane hydrocarbons (NMHC) are the major sulfur and carbon gases transferred between the ocean and the atmosphere. The oceanic concentrations of these species are determined by numerous biogeochemical and physical processes. In the equatorial Pacific Ocean these processes cause these biogenic trace gases to be supersaturated with respect to the overlying atmosphere which results in a net flux from the ocean to the atmosphere [Lamontagne et al., 1974; Swinnerton et al., 1976; Bates et al., 1987; Feely et al., 1987; Donahue and Prinn, this issue].

The third Soviet-American Gases and Aerosols (SAGA 3) experiment (February to March 1990) provided an opportunity to determine the partial pressures of DMS, CH₄, CO, and CO₂ in surface seawater and the overlying atmosphere of the central equatorial Pacific Ocean (NMHC are reported elsewhere, Donahue and Prinn [this issue]). The measurements were made between 15°N and 10°S along three meridional transects at 145°, 155°, and 165°W and along the diagonals connecting these transects (Figure 1). Since none of the gases showed any significant longitudinal gradient, we report here the latitudinal average mixing ratios, partial pressures, or concentrations from the five transects. The data are then used to calculate the fluxes of these gases to the atmosphere. This data set permits an interesting comparison of the relative magnitudes of the ocean-atmosphere fluxes of the dominant sulfur and carbon

species and also provides the necessary fluxes for atmospheric sulfur cycle [Huebert et al., this issue] and atmospheric marine photochemical [Thompson et al., this issue] models.

METHODS

Sampling

Gas partial pressures were determined continuously in surface seawater along the cruise track (Figure 1) using two different equilibrator systems designed to partition dissolved gases between seawater and a vapor phase for sampling. Both equilibrators were fed with seawater pumped directly to the laboratory area from an intake located at a 5-m depth near the bow of the ship. The Weiss equilibrator [Butler et al., 1988], used for CH₄, CO, and CO₂ sampling, was constructed from Plexiglas and consisted of a 20-L enclosed headspace continuously showered with 20 L/min of seawater. Every 48 min, approximately 50 ml of gas were withdrawn from the headspace to flush the sample loop and 2 ml were injected for analysis. The Gortex equilibrator, used for DMS sampling, consisted of a 700-ml Teflon reservoir containing 10 m of Teflon (Gortex) tubing perforated with 2-μm-diameter pores. The pores in the tubing allowed gas transfer but prevented liquid transfer due to surface tension of the water. Seawater continuously flowed through the reservoir at 600 ml/min, while DMS-free air entered through the Gortex tubing at 100 ml/min.

Surface seawater temperatures were measured every 3 hours in a sample collected by bucket and continuously in the Weiss equilibrator. On average, the seawater temperature measured in the equilibrator was 0.03°C ± 0.21°C warmer than that measured in the bucket due to heating from the pump and transit through the ship. Because of the uncertainty in the difference between the two measurements, we have not made any corrections to the data for temperature warming. If the warming were indeed 0.03°C, the seawater mixing ratios reported here would be high by 0.12%, 0.05%, 0.04%, and 0.08% for DMS, CH₄, CO, and CO₂, respectively (based on solubilities discussed below). The concentrations and fluxes calculated here also make no attempt to correct for any temperature difference between the 5-m inlet depth and the surface microlayer [Katsaros, 1980].

Air samples for CH₄, CO, and CO₂ were pulled from the bow of the ship, 10 m above the sea surface, to the oceanographic laboratory (approximately 40 m) through plastic-coated aluminum tubing (Dekoron) at a flow rate of 10 L/min.

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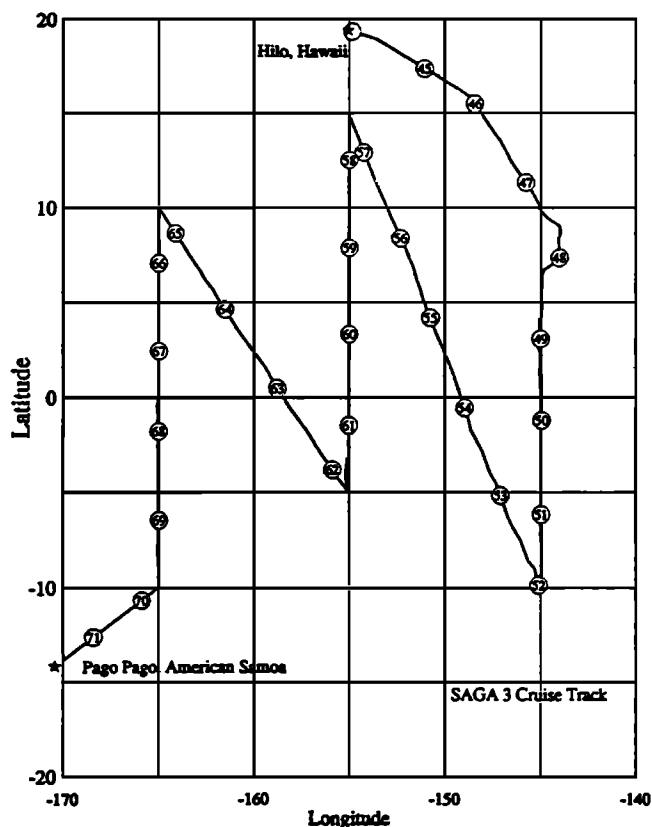
Fig. 1. The third Soviet-American Gases and Aerosols (SAGA 3) cruise track aboard the R/V *Akademik Korolev* (February 13 to March 13, 1990). The day of the year is indicated along the track. Latitude refers to degrees north. Negative longitude is degrees west.

Dekoron tubing was also used to connect the Weiss equilibrator to the analytical system. Laboratory tests have shown that there is no production or loss of these carbon species in the Dekoron tubing.

Mixing Ratio Measurements

Dimethylsulfide. DMS mixing ratios were measured with the ECD-S system [*Johnson and Lovelock*, 1988] which, after chromatographic separation, fluorinates sulfur compounds to SF_6 and then detects them with a conventional electron capture detector. Air samples from the air-sampling line [*Huebert et al.*, this issue], the Gortex equilibrator, or a standard stream were dried in a Teflon loop immersed in cold alcohol (−40°C) and drawn into a 2-ml sample loop connected to an automated Valco sample valve. Sulfur compounds were separated at 60°C on a Carbopak B/XE-60/H₃PO₄ chromatographic column using N_2 at 40 ml/min as the carrier gas. The column effluent was mixed with 20 ml/min of a 300 parts per million by volume (ppmv) F_2 in N_2 mixture (created in a permeation source) and passed through a silver catalyst column where the sulfur compounds were fluorinated. Following the silver catalyst, 1 ml/min of H_2 was added to the flow stream before entering a palladium on alumina column where the excess F_2 was converted to HF. Both the Ag and Pd columns were at 150°C. The gas flow then entered a conventional [63]Ni, electron capture detector attached to a HP3393 integrator-computer. The system was automated to run unattended for periods of 4 to 8 hours with alternating injections every 10 min of air, standard, equilibrated air, and standard.

Standards were generated by flowing DMS-free air over a low-loss rate (3.7 ng S/min) permeation tube that was held at a constant temperature of 40 ± 0.1°C. The permeation rate of the tube was calibrated with a higher-loss rate permeation tube whose weight was calibrated gravimetrically. A modified version of this system, calibrated with the same high-loss rate permeation tube was used successfully in the NASA CITE 3 sulfur intercomparison [*Gregory et al.*, 1993].

Configured for SAGA 3, the ECD-S system had a lower limit of detection of 20 fmol or 10 pmol/L (250 ppt). The instrument accuracy and precision for DMS, as determined on CITE 3, was ±12% and ±10%, respectively [*Johnson and Bates*, 1993].

Methane, carbon monoxide, carbon dioxide. CH₄, CO, and CO₂ mixing ratios were measured with an automated, temperature-controlled, gas chromatographic system containing both a flame ionization detector (FID) and a mercury bed detector (MBD) [K.C. Kelly et al., manuscript in preparation, 1992). Air samples from the bow air-sampling line, the Weiss equilibrator, or a standard gas stream were dried using phosphorous pentoxide and drawn into a 2-ml sample loop connected to an automated sample valve. The three carbon gases were separated and isolated using a series of five columns with CO valved to the MBD, CH₄ valved directly to the FID, and CO₂ catalytically reduced to CH₄ and then valved to the FID. The signals from the detectors were digitized and quantified by a HP3392 integrator-computer. The system was automated with a Carle series 400 controller and ran unattended with alternating injections of air, standard 1, equilibrated air, and standard 2 every 12 min.

Standards were dried, whole air mixtures contained in aluminum cylinders. The standards were calibrated both before and after the cruise by National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL). CH₄ values are referenced to the Rasmussen scale [*Rasmussen and Lovelock*, 1983], CO mixing ratios are reported on a calibration scale developed at CMDL [*Novelli et al.*, 1991], and CO₂ data are reported in the World Meteorological Organization (WMO) X85 scale [*Thoning et al.*, 1987]. The standard mixing ratios were chosen to bracket the ambient air and seawater mixing ratios. Since our 3 ppmv CO standard is higher than the CMDL standard scale, this standard (used for seawater CO measurements) had the highest uncertainty in its accuracy (±10%). The accuracies of the other standards, as quoted by CMDL, were ±1.5%, ±2%, and ±0.6% for CH₄, CO, and CO₂, respectively. During this cruise the instrument precision, as determined by the average percent standard deviation of the standard response over a 6-hour period, was ±1.8% for CH₄ at 1617 and 2024 parts per billion by volume (ppbv), ±1.5% for CO at 2900 ppbv, ±3.9% for CO at 71 ppbv, and ±0.87% for CO₂ at 347 and 460 ppmv.

Data Reduction and Flux Calculations

Air-sea transport velocity (kₗ). The air-sea fluxes for the four gases were calculated from the measured mixing ratios, gas solubilities and diffusivities, and an empirically derived transport velocity (kₗ). A value for kₗ was calculated for each gas concentration measurement using local wind speeds measured aboard the ship and the wind speed/transfer velocity relationships derived by *Liss and Merlivat* [1986].

for ws ≤ 3.6, $k_l = (0.41 * ws)(Sc/600)^{-0.66}$

for $3.6 < ws \geq 13$, $k_l = (0.68 * ws - 2.31)(Sc/600)^{-0.5}$

for $ws > 13$, $k_l = (1.42 * ws - 11.8)(Sc/600)^{-0.5}$

These relationships give a k_l (m/d) as a function of wind speed (ws in m/s) at 10 m above sea level for a soluble gas at 20°C with a Schmidt number (Sc, defined as the kinematic viscosity of seawater divided by the gas diffusivity) of 600. The local wind speed measured aboard *Akademik Korolev* at 22 m above sea level was normalized to 10 m assuming a logarithmic wind profile and a drag coefficient of 1.5×10^{-3} [*Liss and Merlivat*, 1986]. This reduced the local wind speeds by approximately 8%. The resulting k_l value was then adjusted using the local seawater temperature and calculated seawater gas diffusivities by assuming that k_l was proportional to $Sc^{-0.66}$ at wind speeds ≤ 3.6 m/s and to $Sc^{-0.5}$ at higher wind speeds [*Liss and Merlivat*, 1986]. Gas diffusivities in freshwater [*Jahne et al.*, 1987, for CH₄ and CO₂; *Saltzman et al.*, 1993, for DMS; *Wise and Houghton*, 1968, for CO] were reduced by 6% to correct for seawater [*Jahne et al.*, 1987]. The gas diffusivities used in these calculations at a temperature of 20°C and a salinity of 35 ppt resulted in Schmidt numbers of 934, 680, 580, and 660 for DMS, CH₄, CO, and CO₂, respectively.

Although the calculations are straightforward, there are still large uncertainties in the resulting values of k_l. While the *Liss and Merlivat* [1986] wind speed/transfer velocity relationship has recently been supported by dual tracer techniques [*Watson et al.*, 1991], other studies suggest that this relationship underestimates the flux by as much as a factor of 2 [*Smethie et al.*, 1985; *Erickson*, 1989; *Tans et al.*, 1990; *Wanninkhof*, 1992]. These differences are in part due to the wind fields used in the calculations. Since many of the wind speed/transfer velocity relationships are nonlinear, transfer velocities calculated with long-term average winds will generally be lower than those obtained using short-term variable winds [*Wanninkhof*, 1992]. The choice of wind fields depends upon the available data and the scientific objective. Studies aimed at obtaining a large-scale (ocean basin or global) average gas flux by necessity use long-term average winds [*Bates et al.*, 1987; *Tans et al.*, 1990; *Murphy et al.*, 1991]. In analyzing the SAGA 3 data, we were interested in calculating and comparing the instantaneous flux of DMS, CH₄, CO, and CO₂ within the study region. For this purpose we have chosen to use the local ship winds (Figure 2a) and the *Liss and Merlivat* [1986] wind speed/transfer velocity relationships. Average fluxes calculated for the SAGA 3 data using shipboard winds and the quadratic dependence of gas exchange on wind speed suggested by *Wanninkhof* [1992] were, on average, 77% higher than those calculated using *Liss and Merlivat* [1986].

Wind speed is only one factor that influences gas transport. It is clear that boundary layer stability, surfactants, bubbles, fetch, and chemical/biochemical reactions in the ocean surface layers all play a role in gas transport [*Wanninkhof*, 1992]. Laboratory studies combined with remotely sensed ocean whitecap coverage may eventually lead to more accurate estimates of gas transfer [*Wanninkhof and Bliven*, 1991; *Asher et al.*, 1991]. At this time however, despite the uncertainties, wind speed continues to be the most widely used parameter to estimate gas transfer rates.

The standard deviations reported for the fluxes calculated here reflect the variability in the gas mixing ratios and wind speeds encountered during SAGA 3. The standard deviations
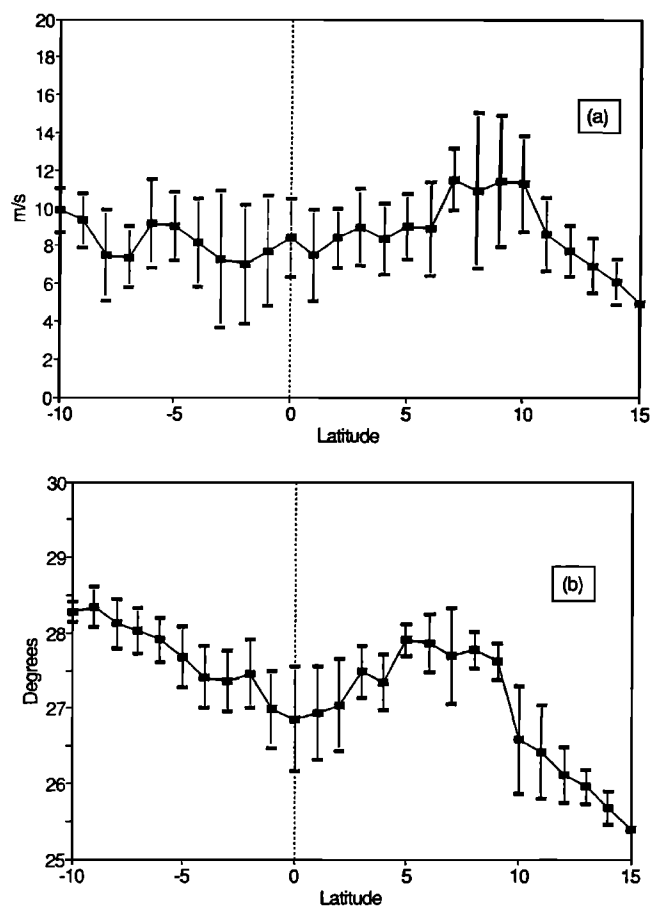

Fig. 2. (*a*) Wind speed at 22 m above sea level in m/s and (*b*) surface seawater temperature in °C averaged over the five latitudinal transects (145°W to 165°W) into 1° bins. The vertical bars indicate 1 s.d.

do not take into account the uncertainties in the wind speed/gas transfer relationships.

Dimethylsulfide. The partial pressures of DMS in surface seawater were converted to units of nmol/L using surface seawater temperatures and the solubility relationship of *Dacey et al.* [1984]. Previous simultaneous measurements using this technique and the more conventional gas stripping method [*Quinn et al.*, 1990] have agreed to within 10% in the temperature range observed during SAGA 3 (25.5°–28.5°C) (T. S. Bates and J. E. Johnson, unpublished data, 1988). DMS fluxes were calculated as the product of the seawater DMS concentration and the transport velocity (k_l) [*Bates et al.*, 1987]. The concentration and flux values were then combined into 1° averages as a function of latitude.

Methane, carbon monoxide, carbon dioxide. The data were first visually filtered to eliminate any episodes of ship contamination. There were approximately 10 such episodes during the cruise which were quite evident from the extremely high CO values (greater than 10 times ambient). The mixing ratios of the carbon gases in both air and equilibrator samples were then computed based on peak height (CH₄) or peak area (CO and CO₂) and a 6-hour running-mean single-point standard. These dry-air mixing ratios were averaged into 2-hour intervals and used to calculate ΔpCH₄, ΔpCO, and ΔpCO₂ in units of microatmospheres,

$$\Delta pC = (P_a - P_w) [(X)_e - (X)_a]$$

where ΔpC is the difference in the air and seawater partial pressures of the three carbon gases, P_a is the atmospheric pressure, P_w is the saturation water vapor pressure, and X_a and X_e are the mixing ratios of gas in the atmosphere and equilibrator air, respectively. P_w was calculated at the local sea surface temperature (Figure 2b) and a salinity of 35 ppt, according to Weiss and Price [1980].

Gas solubilities in mol/l/atm were calculated for each value using the local temperature, a salinity of 35 ppt and the equilibrium solubility equations of Weiss [1974] and Wiesenburg and Guinasso [1979]. The air-sea exchange was then calculated as the product of the ΔpC, equilibrium solubility, and the transfer velocity (k_l).

RESULTS AND DISCUSSION

Dimethylsulfide

DMS is produced from the enzymatic cleavage of dimethylsulfonium propionate (DMSP), an osmolyte produced by certain phytoplankton species [Dacey and Blough, 1987; Kiene, 1992]. The concentration of DMS in surface seawater appears to be primarily controlled by the biological cycling of DMS and DMSP with biological turnover times of approximately 1–2 days [Kiene and Bates, 1990; Leck et al., 1990; Kiene, 1992]. Seawater DMS concentrations determined during SAGA 3 showed a pronounced latitudinal gradient (Figure 3).
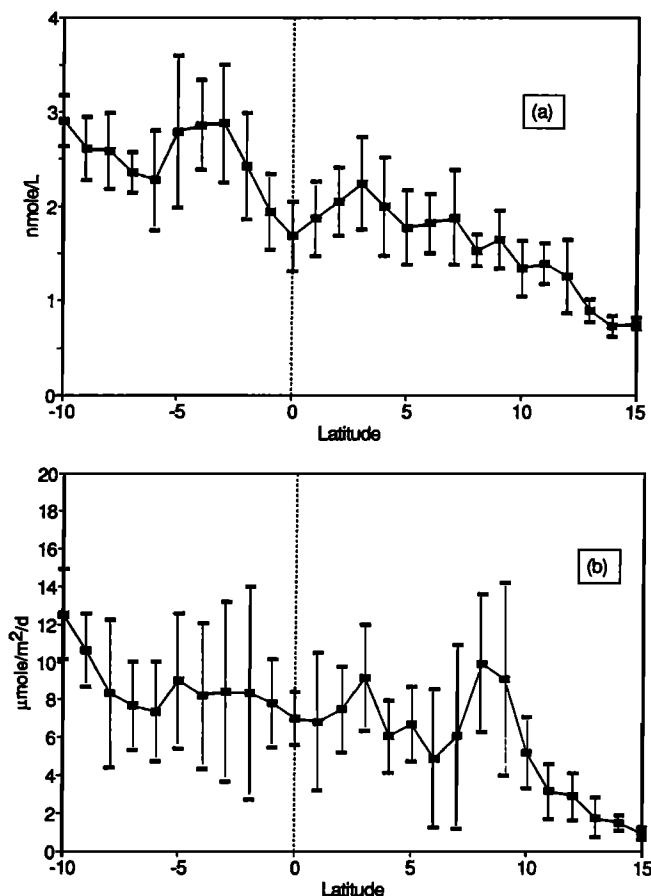

Fig. 3. (a) Surface seawater DMS concentrations in nmol/L and (b) DMS fluxes to the atmosphere in μmol/m^2/d. The concentrations and fluxes were calculated for each individual measurement along the five latitudinal transects (145°W to 165°W) and then averaged into 1° bins with the vertical bars showing 1 s.d.

TABLE 1. Mean Gas Concentrations, Mixing Ratios and/or Partial Pressures and Calculated Air-Sea Fluxes From SAGA 3 (15°N to 10°S, 145°W to 165°W)

	Units	Mean	SD	Max	Min
DMS$_{water}$	nmol/L	2.0	±0.70	4.2	0.6
DMS$_{flux}$					
15°N to 10°S	μmol/m^2/d	7.1	±4.0	21.2	0.0
10°N to 10°S	μmol/m^2/d	7.7	±3.8		
CH$_{4-air}$	ppmv	1.69	±0.022	1.74	1.64
	μatm	1.62	±0.023	1.68	1.57
CH$_{4-water}$	nmol/L	1.81	±0.052	1.96	1.68
	μatm	1.71	±0.038	1.83	1.61
CH$_{4-flux}$					
15°N to 10°S	μmol/m^2/d	0.39	±0.34	2.5	0.0
10°N to 10°S	μmol/m^2/d	0.41	±0.35		
CO$_{air}$	ppbv	76.4	±11.1	105.5	54.5
	μatm	0.079	±0.011	0.110	0.057
CO$_{water}$	nmol/L	1.0	±0.40	2.4	0.39
	μatm	1.30	±0.52	2.98	0.51
CO$_{flux}$					
15°N to 10°S	μmol/m^2/d	4.2	±2.8	20.2	0.0
10°N to 10°S	μmol/m^2/d	4.3	±2.8		
CO$_{2-air}$	ppmv	355.0	±1.2	359.2	352.4
	μatm	341.3	±1.6	346.8	337.8
CO$_{2-water}$	μatm	388.8	±39.8	452.7	319.0
CO$_{2-flux}$					
15°N to 10°S	mmol/m^2/d	5.4	±5.5	19.3	-3.5
10°N to 10°S	mmol/m^2/d	6.3	±5.2		

Average concentrations increased from 1 nmol/L at 15°N to 3 nmol/L at 10°S (Figure 3a) with an average concentration in the study region of 2.0 ± 0.7 nmol/L (Table 1). The range of concentrations observed during SAGA 3 was similar to that previously reported in this region (1 to 4 nmol/L) [Andreae and Raemdonck, 1983; Cline and Bates, 1983; Bates et al., 1987]. Although many of these studies have shown maximum concentrations at or near the equator, our observations of a north-south concentration gradient are similar to those reported by Quinn et al. [1990] along 170°W. Unfortunately, it is difficult to assess whether this concentration gradient is a seasonal feature since all the DMS measurements reported to date in the equatorial Pacific Ocean have been during the northern hemisphere spring.

The flux of DMS to the atmosphere ranged from 1 μmol/m^2/d at 15°N to 12 μmol/m^2/d at 10°S (Figure 3b) with an average of 7.1 ± 4.0 μmol/m^2/d (Table 1). The latitudinal gradient in the flux of DMS generally paralleled the latitudinal concentration gradient except in the region between 8°N and 15°N where the higher wind speeds at 8°N and lower wind speeds at 15°N (Figure 2a) corresponded to higher and lower fluxes, respectively. The fluxes calculated here are in the same range as those calculated by Quinn et al. [1990] at 170°W in 1988 and encompass the average regional flux calculated for this region (approximately 5 μmol/m^2/d) by Bates et al. [1987]. This flux is the beginning of the atmospheric sulfur cycle that is discussed in this issue by Huebert et al. [this issue].

Methane

Methane is produced in surface seawater by bacteria, presumably in zones of very low oxygen concentrations within microparticulates [Scranton and Brewer, 1977; Kiene, 1991]. Biological consumption processes and air-sea exchange balance

this production [*Ward et al.*, 1987] with resulting seawater methane turnover times of months to years [*Kiene*, 1991]. The long turnover times result in fairly uniform seawater CH$_4$ concentrations. The average concentration in the equatorial Pacific (10°N to 10°S) during SAGA 3 was 1.8 ± 0.05 nmol/L (Figure 4*a*, Table 1) with no significant latitudinal or longitudinal variation. The concentrations were slightly higher (1.9 ± 0.05 nmol/L, Figure 4*a*) between 10°N and 15°N due to lower seawater temperatures (Figure 2*b*). *Lamontagne et al.* [1974] found similarly uniform CH$_4$ concentrations in the equatorial Pacific Ocean in 1972. Their average concentration was 1.9 nmol/L.

Atmospheric CH$_4$ mixing ratios measured during SAGA 3 showed a pronounced latitudinal gradient (Figure 4*b*) ranging from 1720 ppb at 15°N to 1660 ppb at 10°S. These mixing ratios are consistent with those measured by NOAA/CMDL on Christmas Island (1.7°N, 157.2°W) and Guam (13.4°N, 144.8°E) (1690 ppb and 1725 ppb, respectively, E. J. Dlugokencky and P. M. Lang, personal communication, 1992, see Figure 4*b*) during February to March 1990.

Although biologically productive coastal areas [*Cline et al.*, 1986] and seas [*Owens et al.*, 1991] exhibit large methane supersaturations, the equatorial Pacific Ocean during SAGA 3 was only slightly supersaturated with respect to the overlying atmosphere. One-degree-averaged data indicated that surface seawater methane was supersatured by a factor of 1.051 ± 0.022 resulting in a small net flux to the atmosphere of 0.39 μmol/m^2/d (Figure 4*c*, Table 1). This supersaturation factor is similar to that obtained by *Ward et al.* [1987] in the western Cariaco Basin (supersaturation factor of 1.036) but significantly less than the open ocean values calculated in the early 1970s by *Lamontagne et al.* [1973] in the Pacific Ocean (supersaturation factor of 1.30; see calculations by *Ehhalt* [1974]) and in 1979 to 1980 by *Conrad and Seiler* [1988] in the Atlantic Ocean (average supersaturation factor of 1.10). The increase in atmospheric methane mixing ratios during the past 20 years (10–18 ppb per year, *Fraser et al.* [1986], *Blake and Rowland* [1986], *Steele et al.* [1987], and *Scheel et al.* [1990]) could account for the decrease in observed methane supersaturations. It has been suggested that rising atmospheric methane concentrations could eventually turn the surface ocean into a methane sink [*Cicerone and Oremland*, 1988]. Although the global accumulation of atmospheric methane has slowed during the 1980s [*Steele et al.*, 1992], the data from SAGA 3 show that the equatorial Pacific Ocean is nearly in equilibrium with the overlying atmosphere.

Carbon Monoxide

Two-hour-averaged seawater CO concentrations ranged from 0.39 to 2.4 nmol/l. The daily averaged concentrations showed the same latitudinal variation as the 2° latitudinally binned data (Figure 5*a*) with the highest concentrations between 3° and 4°S. Slightly higher CO concentrations have been previously observed in this region by *Swinnerton et al.* [1976] (4.5 nmol/L at 6°S) and *Swinnerton and Lamontagne* [1974] (6.2 nmol/L at 10°S). Although *Swinnerton et al.* [1976] attributed this region of high CO concentration to nutrient-rich highly productive seawater from western South America, we saw no correlation of CO concentrations with either surface chlorophyll or nitrate concentrations. The daily average concentrations measured by Swinnerton et al. in the central equatorial Pacific Ocean ranged from 0.9 to 6.2 nmol/l. Although these concentrations are
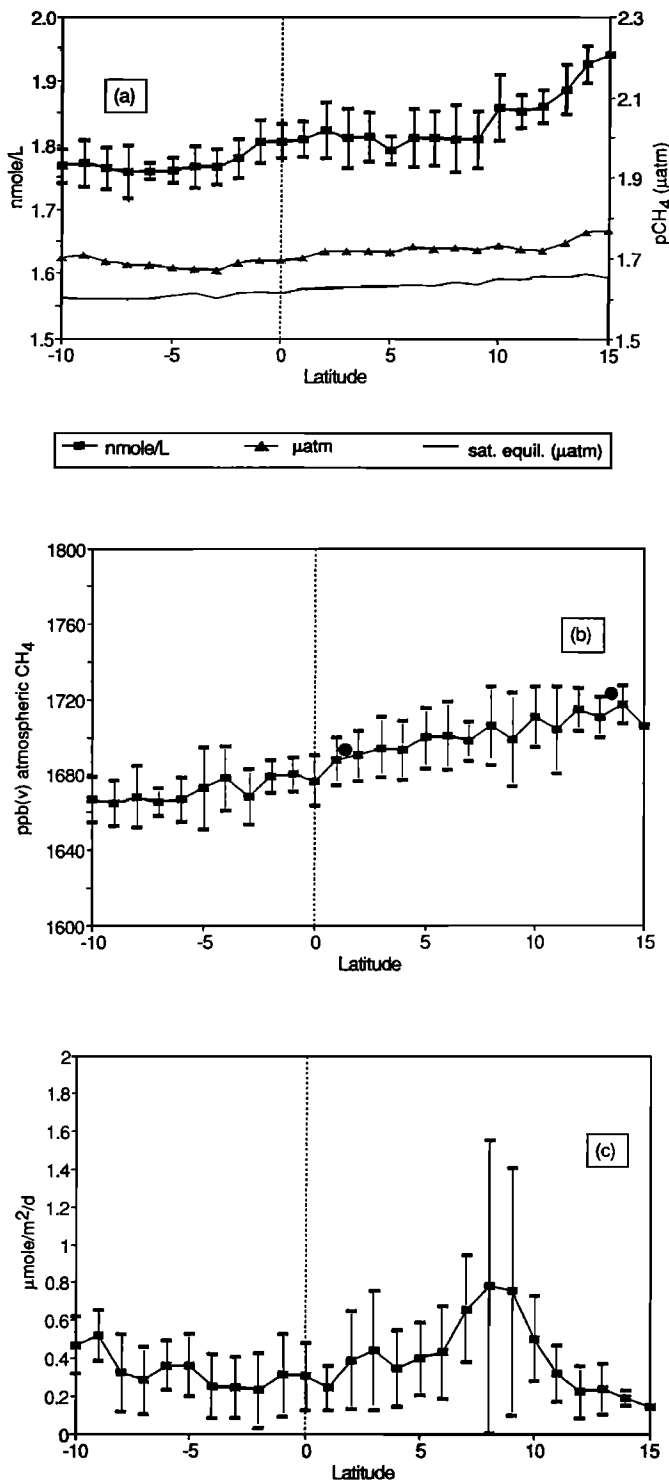

Fig. 4. (*a*) Surface seawater methane concentrations in nmol/L and partial pressures in microatmospheres. The saturated equilibrium partial pressure is also given in microatmospheres. (*b*) Atmospheric methane mixing ratios in parts per billion by volume (ppbv) dry air. The circles are the measured mixing ratios in flask samples taken by National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) at Christmas Island and Guam (E. J. Dlugokencky and P. M. Lang, personal communication, 1992). (*c*) The flux of methane from the ocean to the atmosphere in μmol/m^2/d. The dry-air mixing ratios were averaged into 2-hour intervals and then used to calculate concentrations, partial pressures, and fluxes. The data were then averaged into 1° bins along the five latitudinal transects (145°W to 165°W). The vertical bars show 1 s.d. of the bin-averaged data.
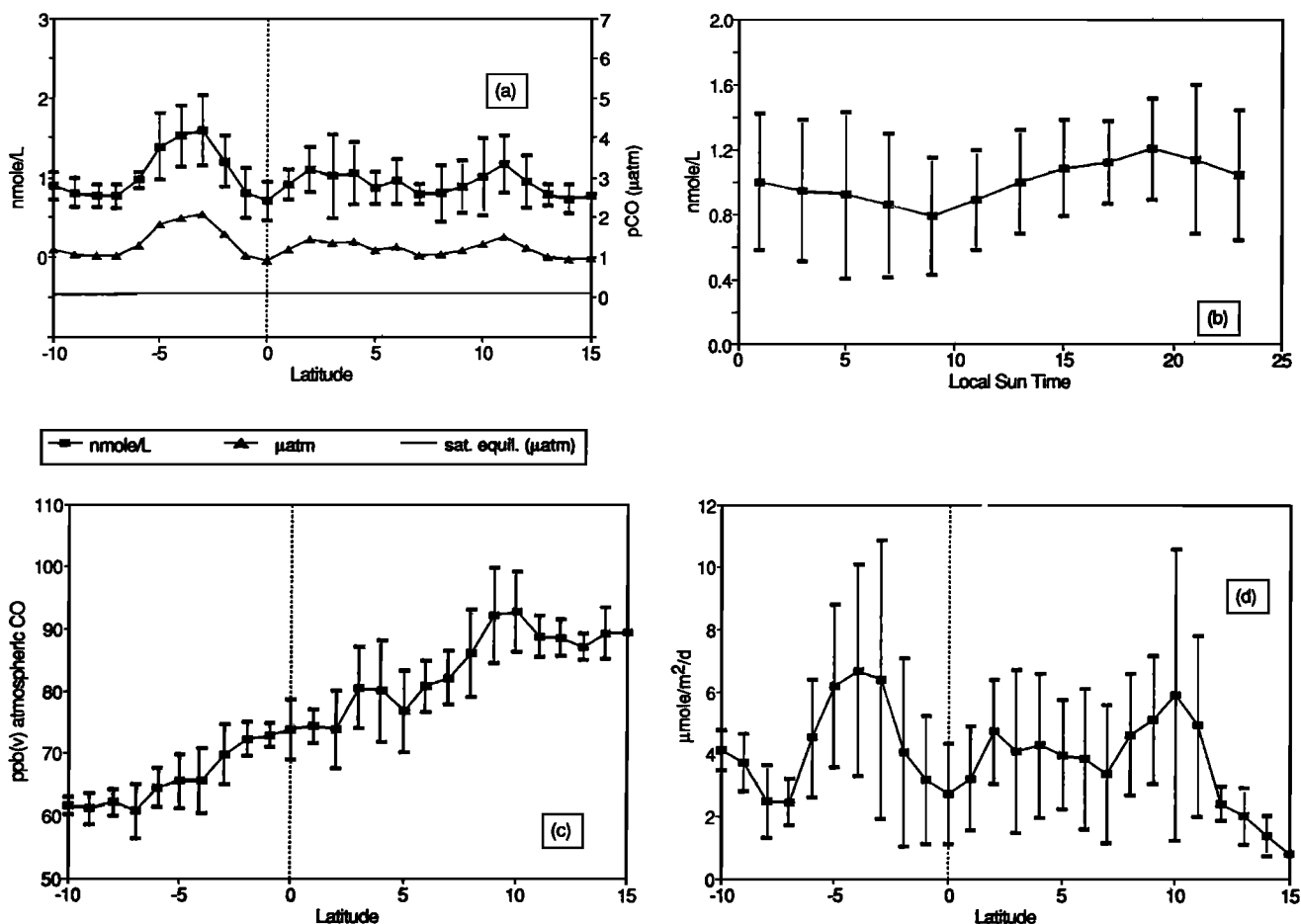
Fig. 5. Surface seawater CO (a) concentrations in nmol/L and partial pressures in microatmospheres. The saturated equilibrium partial pressure is also given in microatmospheres. The diurnal cycle of seawater CO concentrations (b) in nmol/L plotted versus local Sun time. Atmospheric CO mixing ratios (c) in ppbv dry air. The flux of CO from the ocean to the atmosphere (d) in μmol/m^2/d. The dry-air mixing ratios were averaged into 2-hour intervals and then used to calculate concentrations, partial pressures, and fluxes. The data were then averaged into 1° bins along the five latitudinal transects (145°W to 165°W). The vertical bars show 1 s.d. of the bin-averaged data.

generally higher than those reported here, the high dependency of CO seawater concentrations on incident solar radiation and surface wind speeds [Conrad et al., 1982] likely causes large seasonal and annual variations in CO surface seawater concentrations and hence makes comparisons difficult.

Seawater CO concentrations, averaged over the cruise, varied during the day by approximately a factor of 1.5 with the highest concentrations occurring around 1800 LT (Figure 5b). The large standard deviations on these values reflect the combined spatial and temporal variability since the ship was under way during most of each day. The diurnal variation in seawater CO concentrations is a result of UV photochemical production which has been shown to be proportional to the amount of dissolved organic carbon (DOC) [Wilson et al., 1970] and sunlight [Lamontagne et al., 1971; Conrad et al., 1982]. The photochemical production is balanced by the combined effects of microbial consumption [Conrad et al., 1982; Conrad and Seiler, 1980, 1982] and air-sea exchange [Butler et al., 1987; Conrad et al., 1982]. Rate studies in coastal waters (Yaquina Bay) suggest that seawater CO turnover times are of the order of a few hours [Butler et al., 1987]. Similar lifetimes have been estimated by Conrad et al. [1982] based on the diurnal variations in seawater concentrations.

Atmospheric CO has a lifetime of approximately 3 months [IPCC, 1990] which results in less variable concentrations than CO in seawater (Figure 5c). The mixing ratios measured during SAGA 3 showed a strong north-south gradient ranging from 93 ppb in the northern hemisphere to 60 ppb in the southern hemisphere. CO mixing ratios measured during this cruise were approximately 20% lower than the February to March monthly average values measured by NOAA/CMDL on Christmas Island (1.7°N, 157.2°W) and American Samoa (14.2°S, 170.5°E) (97 ppb and 61 ppb, respectively, Novelli et al. [1992]). The range of values measured during February and March 1990 at the two NOAA/CMDL baseline stations, however, do overlap the values measured on board the Akademik Korolev.

CO in surface seawater is supersaturated by approximately a factor of 10 (Figures 5a and 5c) which results in an average net flux of CO to the atmosphere ranging from 0.8 to 6.5 μmol/m^2/d (Figure 5d). Since this flux is primarily controlled by the high seawater CO concentrations, the latitudinal distribution of CO fluxes closely resembles the latitudinal distribution of CO seawater concentrations (Figures 5a and 5d). The fluxes calculated here are much lower than those calculated by Erickson [1989] for this region (approximately 50 μmol/m^2/d). The difference is primarily a result of the

different seawater concentrations used in the two calculations. *Erickson* [1989] calculated seawater CO concentrations based on a relationship between surface solar radiation and surface seawater CO concentrations developed by *Conrad et al.* [1982]. Based on the concentrations reported here and the measurements of both *Swinnerton et al.* [1976] and *Conrad et al.* [1982], this relationship, as interpreted by *Erickson* [1989], appears to overpredict the surface seawater CO concentration by roughly an order of magnitude.

Carbon Dioxide

During non-El Niño years, CO$_2$ in the equatorial Pacific Ocean is supersaturated with respect to the overlying atmosphere [*Keeling et al.*, 1965; *Feely et al.*, 1987]. Although CO$_2$ is biologically cycled within the surface waters, the high CO$_2$ supersaturation in the equatorial Pacific Ocean is a result of more dominant physical processes, namely, the upwelling of low-oxygen, high-nutrient, high-CO$_2$ waters [*Feely et al.*, 1987]. During SAGA 3, the partial pressure of CO$_2$ in surface waters along the cruise track reached 452 µatm (Table 1) with supersaturations of as high as 32% above equilibrium (equator at 145°W). North of 9°N, CO$_2$ in surface waters was undersaturated with respect to the overlying atmosphere (Figure 6a). These seawater partial pressures and deviations from equi-

librium (Figure 6c) are consistent with values previously reported for this area [*Feely et al.*, 1987; *Murphy et al.*, 1991; *Inoue and Sugimura*, 1992]. Also apparent in these data is the growth of atmospheric CO$_2$ in the equatorial Pacific which has risen from approximately 345 ppmv in March 1984 [*Feely et al.*, 1987] to 355 ppmv in March 1990. This growth rate (1.6 ppmv/yr) is equivalent to the observed average global increase for the decade 1980 to 1989 [*IPCC*, 1990]. The atmospheric CO$_2$ mixing ratios measured on SAGA 3 are consistent with those measured by NOAA/CMDL on Christmas Island (1.7°N, 157.2°W) and Guam (13.4°N, 144.8°E) (355.3 ppmv and 355.9 ppmv, respectively, T. Conway, personal communication, 1992; see Figure 4b) during February to March 1990.

The ΔpCO_2 in the equatorial Pacific Ocean results in fluxes to the atmosphere ranging from -3.5 mmol/m^2/d to 19.3 mmol/m^2/d (Figure 6d, Table 1). The average flux between 10°N and 10°S, was 6.3 ± 5.2 mmol/m^2/d. This is slightly higher than that calculated for the same region by *Smethie et al.* [1985] (5.7 mmol/m^2/d) and *Feely et al.* [1987] (3.9 mmol/m^2/d) but still well within the uncertainties of the calculated fluxes.

Gas Comparisons and Summary

Although DMS, CH$_4$, CO, and CO$_2$ are all involved in the biological cycles of sulfur and/or carbon in the surface ocean,
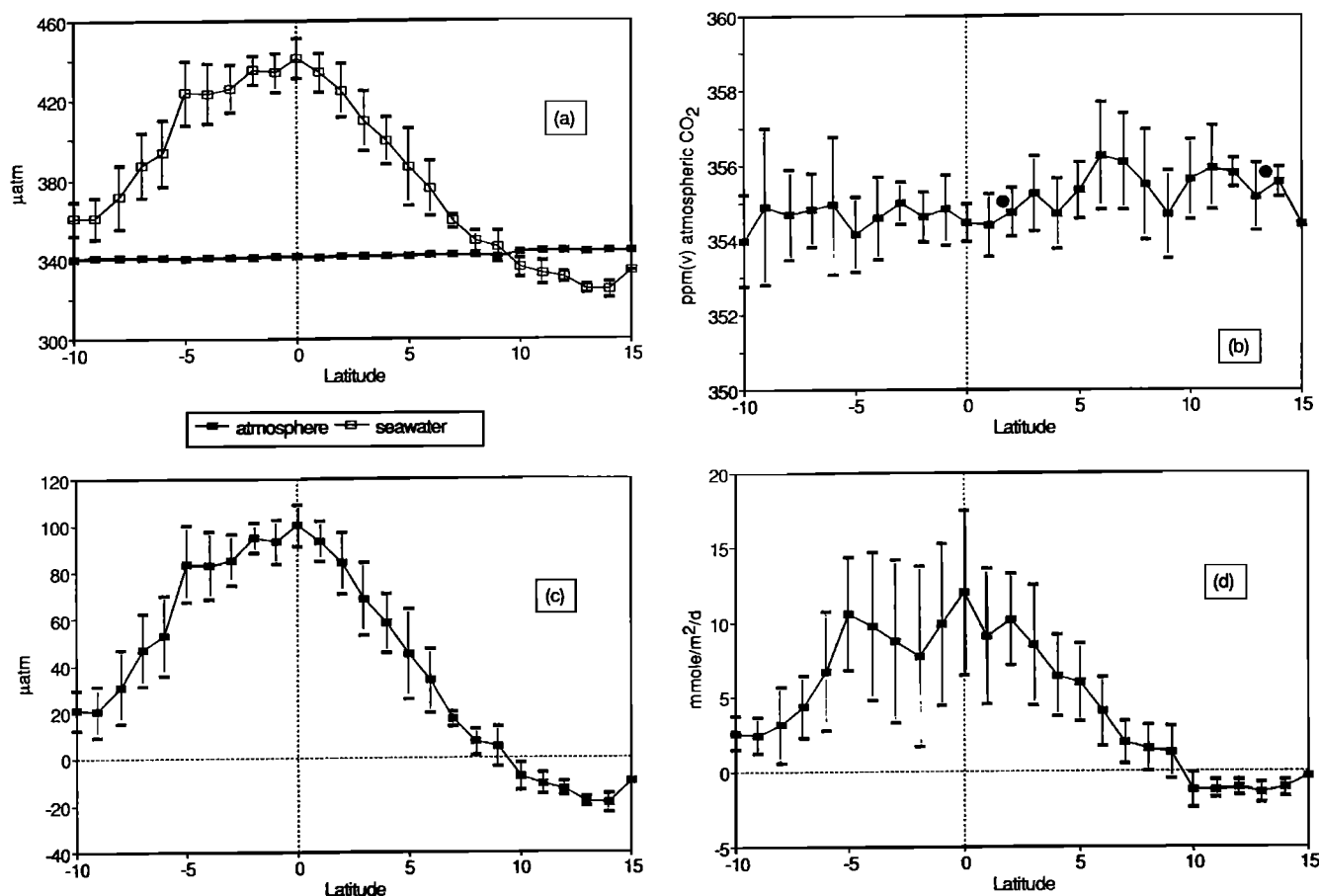

Fig. 6. Surface seawater and atmospheric CO$_2$ partial pressures (a) in microatmospheres. Atmospheric CO$_2$ mixing ratios (b) in parts per million by volume (ppmv) dry air. The circles are the measured mixing ratios in flask samples taken by NOAA/CMDL at Christmas Island and Guam (T. Conway, personal communication, 1992). Delta pCO$_2$ (seawater equilibrated air–atmospheric air) (c) in microatmospheres. The flux of CO$_2$ from the ocean to the atmosphere (d) in mmol/m^2/d. The dry-air mixing ratios were averaged into 2-hour intervals and then used to calculate partial pressures and fluxes. The data were then averaged into 1° bins along the five latitudinal transects (145°W to 165°W). The vertical bars show 1 s.d. of the bin-averaged data.

the latitudinal distributions of these gases in surface seawater are quite different. The differences reflect the dominant processes controlling their seawater concentrations and lifetimes. The production of DMS is species specific and requires enzymatic cleavage of its precursor DMSP. The photochemical production of CO in surface waters depends on the amount of DOC and sunlight. Both of these gases are short-lived (hours-days) in surface seawater as a result of microbial consumption. Although the highest seawater concentrations of both gases were found around 4°S (Figures 3a and 5a), average DMS concentrations steadily increased from 15°N to 10°S (Figure 3a), whereas there was no significant latitudinal gradient in the average CO concentrations (Figure 5a). Overall, the seawater concentrations of DMS and CO were more variable than either CH_4 or CO_2. Both CH_4 and CO_2 are much longer lived (months) and hence the seawater concentrations are more uniform. Methane concentrations in surface seawater varied by less than 2% throughout the cruise track (Figure 4a). CO_2, although a product of biological respiration, is strongly controlled in the equatorial Pacific Ocean by the physical process of upwelling. Hence the latitudinal distribution of seawater CO_2 concentrations (Figure 6a) is much different than DMS, CH_4, and CO.

The atmospheric mixing ratios of CH_4, CO, and CO_2 all decrease from 15°N to 10°S (Figures 4b, 5c, and 6b) since the major sources of these gases are anthropogenic emissions in the northern hemisphere. The magnitude of the north-south gradients is a function of the atmospheric lifetime of the gas, the time of the year, and the relative strengths of the sources and sinks in each hemisphere. The gradients in the mixing ratios between 15°N and 10°S ranged from ≈40% for CO, to ≈3% for CH_4, to ≈0.3% for CO_2.

In the central equatorial Pacific, there is a net flux of DMS, CH_4, CO, and CO_2 from the ocean to the atmosphere (Table 1). The fluxes presented here are based on the wind speed/transfer velocity relationships of Liss and Merlivat [1986] and hence are probably lower estimates. Fluxes calculated using the wind speed/transfer velocity relationship of Wanninkhof [1992] were about 77% higher than those calculated using Liss and Merlivat [1986] under the conditions encountered during SAGA 3. The molar fluxes of DMS and CO are similar (≈5 $\mu mol/m^2/d$ based on Liss and Merlivat [1986]) and are about an order of magnitude greater than the molar flux of CH_4 and 3 orders of magnitude less than the molar flux of CO_2. The average flux of CO_2 from the ocean to the atmosphere in the equatorial Pacific (6.3 $mmol/m^2/d$ from 10°S to 10°N, Table 1) is ≈6 times higher than the downward biological carbon flux out of the surface ocean, as measured by Dymond and Collier [1988] in sediment traps at 1100-m depth. Thus air-sea exchange is a significant oceanic sink for carbon in the equatorial Pacific.

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