

## A reevaluation of the open ocean source of methane to the atmosphere

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**Abstract.** Seawater and atmospheric methane (CH<sub>4</sub>) mixing ratios were measured on five cruises throughout the Pacific Ocean from 1987 to 1994 to assess the magnitude of the ocean-atmosphere flux. The results showed consistent regional and seasonal variations with surface seawater concentrations ranging from 1.6 to 3.6 nM and saturation ratios ranging from 0.95 to 1.17. The equatorial Pacific Ocean was supersaturated with respect to atmospheric CH<sub>4</sub> partial pressures, while areas outside the tropics often were undersaturated during fall and winter. Although atmospheric CH<sub>4</sub> mixing ratios over the North Pacific during April increased 3.4% from 1988 to 1993, the saturation ratios remained constant. Based on the concentration fields, the data were divided into two seasons and 10 latitude zones from 75°S to 75°N. Using monthly Comprehensive Ocean-Atmosphere Data Set (COADS) wind and surface seawater temperature data and the *Wanninkhof* [1992] wind speed/transfer velocity relationship, the calculated zonal average fluxes ranged from -0.1 to 0.4 μmol m<sup>-2</sup> d<sup>-1</sup>. The combined seasonal and zonal fluxes result in a total global ocean-to-atmosphere flux of 25 Gmol yr<sup>-1</sup> (0.4 Tg CH<sub>4</sub> yr<sup>-1</sup>), which is an order of magnitude less than previous estimates [Intergovernmental Panel on Climate Change (IPCC), 1994]. The estimated uncertainty in this number is approximately a factor of 2.

### Introduction

Methane (CH<sub>4</sub>) is a potent greenhouse gas and plays a major role in both tropospheric and stratospheric chemistry [Cicerone and Oremland, 1988; Crutzen and Zimmerman, 1991; Intergovernmental Panel on Climate Change (IPCC), 1994]. Its presence in the troposphere affects the Earth's radiation balance, tropospheric ozone concentrations, and the oxidative capacity of the atmosphere. Recent evidence has shown that the tropospheric concentration of CH<sub>4</sub> has changed dramatically over time. Ice core data suggest the atmospheric mixing ratio of CH<sub>4</sub> varied from 300 to 800 ppb during the 40,000 years before the present industrial period [Chappellaz *et al.*, 1993]. During the past 150 years, atmospheric CH<sub>4</sub> mixing ratios have increased to about 1700 ppb as a result of anthropogenic activities [Rasmussen and Khalil, 1984; Steele *et al.*, 1987; Blake and Rowland, 1988; Etheridge *et al.*, 1992; Dlugokencky *et al.*, 1994b]. The globally averaged atmospheric CH<sub>4</sub> growth rate slowed during the 1980s [Steele *et al.*, 1992; Khalil *et al.*, 1993] and then dropped abruptly in 1992 from 11.3 ± 0.2 to 4.7 ± 1.0 ppb yr<sup>-1</sup> [Dlugokencky *et al.*, 1994a]. Explanations for these changes are ambiguous due to uncertainties in the atmospheric CH<sub>4</sub> budget.

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Better estimates of the sources and sinks of CH<sub>4</sub> are needed to understand the temporal trends in atmospheric CH<sub>4</sub> concentrations, to predict future concentrations and climatic impacts, and to provide a basis for strategies to reduce emissions of greenhouse gases.

The surface open ocean is generally slightly supersaturated with respect to atmospheric CH<sub>4</sub> and is thus a source of CH<sub>4</sub> to the atmosphere [Lamontagne *et al.*, 1971, 1973, 1974; Conrad and Seiler, 1988; Bates *et al.*, 1993; Tilbrook and Karl, 1995]. Maximum water column CH<sub>4</sub> concentrations often are found at the pycnocline (50 to 150 m) and can be 2 to 3 times higher than surface water concentrations [Lamontagne *et al.*, 1973; Scranton and Brewer, 1977; Burke *et al.*, 1983]. CH<sub>4</sub> is produced in seawater by bacteria in the digestive tracts of zooplankton [Traganza *et al.*, 1979; Bianchi *et al.*, 1992; Marty, 1993; de Angelis and Lee, 1994] and released into the water column from sinking particles [Karl and Tilbrook, 1994]. The methanogens also appear to be zooplankton species-specific [de Angelis and Lee, 1994], which further contributes to the lack of a consistent correlation between seawater CH<sub>4</sub> concentrations and routinely measured biological parameters [Burke *et al.*, 1983]. CH<sub>4</sub> production in surface seawater is balanced by microbial oxidation [Ward *et al.*, 1987; Jones, 1991] and air-sea exchange. Open-ocean turnover times with respect to biological oxidation are of the order of years [Ward *et al.*, 1987; Jones, 1991; Kiene, 1991], which suggests that air-sea exchange is the major sink for seawater CH<sub>4</sub>.

Early estimates of the open ocean source of CH<sub>4</sub> to the atmosphere were in the range of 250 to 420 Gmol yr<sup>-1</sup> (10<sup>9</sup> mol) [Ehhalt, 1974], or roughly 1% of the total natural and anthropogenic sources [IPCC, 1994]. Two recent reevaluations calculate open ocean sources of 230 Gmol yr<sup>-1</sup> [Lambert and Schmidt, 1993] and 180 to 280 Gmol yr<sup>-1</sup> [Bange *et al.*, 1994]. Although these values are consistent, they are derived from a limited

database and neglect the seasonal variability of the  $\text{CH}_4$  saturation in the surface ocean.

In an effort to reassess the ocean-atmosphere flux of  $\text{CH}_4$ , we have made over 2100 measurements of  $\text{CH}_4$  mixing ratios in surface seawater and the overlying atmosphere on five latitudinal transects in the Pacific Ocean during the past 8 years (Figure 1, Table 1). Based on the seasonal and regional distributions of these data, we have divided the ocean into 10 latitudinal zones and two seasons and recalculated the open-ocean source of  $\text{CH}_4$  to the atmosphere. The complete  $\text{CH}_4$  data set is available via the internet at <http://saga.pmel.noaa.gov>.

## Methods

### Sampling

Surface seawater entered the ship via a forward intake line located approximately 5 m below the water line ( $5 \pm 5$  m, depending on sea state). The water was pumped at a high flow rate (approximately  $100 \text{ L min}^{-1}$ ) to an equilibrator system designed to partition dissolved gases between seawater and a vapor phase for sampling. The plexiglass equilibrator, designed by R. Weiss [Butler *et al.*, 1988; J. Johnson *et al.*, manuscript in preparation, 1995], consisted of a 20-L enclosed headspace continuously showered with a  $15\text{--}20 \text{ L min}^{-1}$  flow of seawater. Every 48 min (1987–1990) or 60 min (1992–1994), approximately 50 mL of gas were drawn from the headspace to flush the sample loop, after which a 2-mL (1987–1990) or 3-mL (1992–1994) sample was injected into the analytical system for analysis. Under these flow conditions the equilibrium time for methane in the equilibrator was approximately 60 min (J. Johnson *et al.*, manuscript in preparation, 1995). Daily field comparisons from  $14^\circ\text{N}$  to  $54^\circ\text{N}$  during the end of the Radiatively Important Trace Species (RITS) 93 cruise showed that the equilibrator sampling technique for  $\text{CH}_4$  produced results equivalent to those of a standard purge and trap technique to within the precision of the analyses (J. Johnson *et al.*, manuscript in preparation, 1995).

Air samples were pumped from the bow of the ship, 10 m above the sea surface (1987–1990) or the top of the aerosol sampling mast, 20 m above the sea surface (1992–1994), to the oceanographic laboratory (approximately 40 m) through aluminum tubing with an inner plastic coating (Dekoron) at a flow rate of  $8\text{--}10 \text{ L min}^{-1}$ . Dekoron tubing was also used to connect the equilibrator to the analytical system. Laboratory tests showed that there was no production or loss of  $\text{CH}_4$  in the Dekoron tubing.

Surface seawater temperature and salinity were measured with a thermosalinograph located at the seawater intake in the ship's hull. The temperatures in the equilibrator were measured using mercury thermometers and thermistors to an accuracy of  $0.1^\circ\text{C}$ . An analysis of the temperature data from 1987–1989 has been reported elsewhere [Murphy *et al.*, 1993]. In 1993 and 1994, the water temperatures measured in the equilibrator were on average  $0.26^\circ\text{C}$  warmer than the intake water temperature due to heating from the pump and transit through the piping to the equilibrator.

### Mixing Ratio Measurements

$\text{CH}_4$  mixing ratios were measured with an automated, temperature controlled, gas chromatographic system containing both a flame ionization detector (FID) and a hot mercuric oxide reduction detector (MBD). Samples from the air sampling line, the equilibrator, and a standard gas stream were dried using phosphorous pentoxide (1987–1990) or magnesium perchlorate (1992–1994) and drawn into a sample loop connected to an automated sample valve.  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  were separated and isolated using a series of five columns with  $\text{CO}$  valved to the MBD,  $\text{CH}_4$  valved directly to the FID and  $\text{CO}_2$  catalytically reduced to  $\text{CH}_4$  and then valved to the FID [Weiss, 1981]. The flame of the FID was fueled by  $\text{H}_2$  and a mixture of 40%  $\text{O}_2$  in  $\text{N}_2$ . The signals from the detectors were digitized and quantified by a HP3392 integrator-computer (1987–1990) or an E-Labs chromatography system (1992–1994). The sampling/GC/

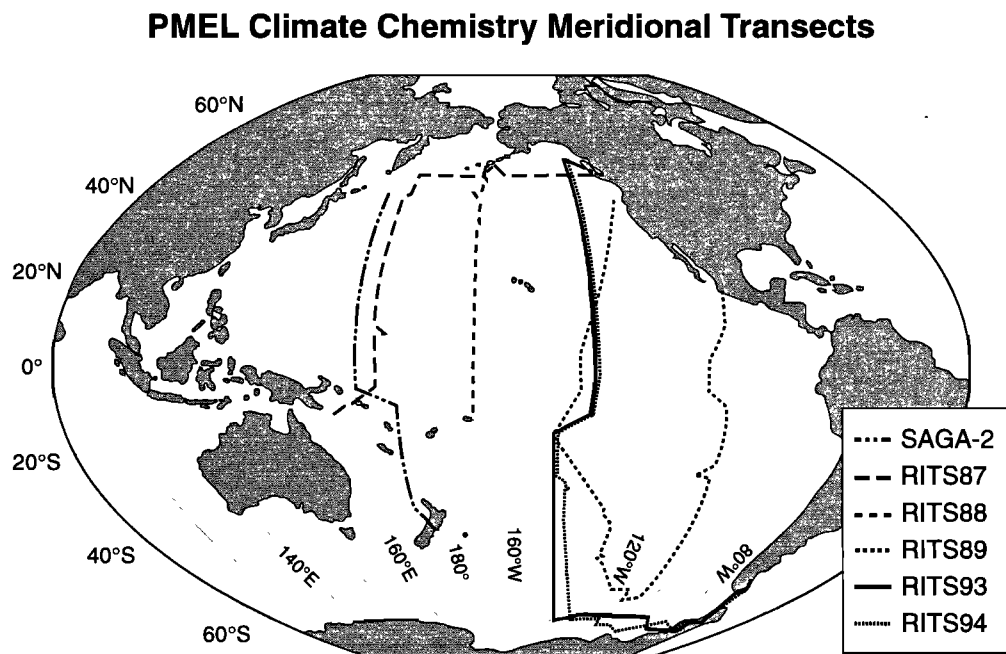


Figure 1. PMEL atmospheric climate/chemistry meridional cruise tracks.

**Table 1.** PMEL Atmospheric Climate/Chemistry Meridional Cruises, 1987–1994

Cruise and Ship	Date	Location
1. SAGA 1987 ( <i>Akademic Korolev</i> ) (SAGA 2)	May 2, 1987	Hilo, Hawaii
	May 12, 1987	Kamchatka, Russia
	June 8–12, 1987	Wellington, New Zealand
	June 26, 1987	29°S, 90°E
	July 6, 1987	Singapore
2. RITS 1987 ( <i>Oceanographer</i> )	July 13, 1987	Townsville, Australia
	August 16, 1987	50°N, 168°E
	August 29, 1987	Seattle, Washington
3. RITS 1988 ( <i>Oceanographer</i> )	April 6, 1988	Dutch Harbor, Alaska
	May 5, 1988	American Samoa
4. RITS 1989 ( <i>Discoverer</i> )	February 13, 1989	Manzanillo, Mexico
	March 1, 1989	Easter Island
	March 15, 1989	60°S, 106°W
	April 2–7, 1989	Papeete, Tahiti
	April 20, 1989	Seattle, Washington
7. RITS 1993 ( <i>Surveyor</i> )	March 20, 1993	Punta Arenas, Chile
	March 24–25, 1993	Palmer Station, Antarctica
	April 1, 1993	68°S, 140°W
	April 15–19, 1993	Papeete, Tahiti
	May 4, 1993	54°N, 140°W
8. RITS 1994 ( <i>Surveyor</i> )	May 7, 1993	Seattle, Washington
	November 20, 1993	Seattle, Washington
	November 23, 1993	55°N, 140°W
	December 13–17, 1993	Papeete, Tahiti
	December 28, 1993	68°S, 130°W
	January 3–4, 1994	Palmer Station, Antarctica
	January 7, 1994	Punta Arenas, Chile

integrator system was automated with a Carle Series 400 Controller and ran with alternating injections of air, standard 1, equilibrated air, and standard 2 every 12–15 min. In this configuration at least one air and one seawater sample were run each hour. The instrument was optimized for CO analysis [Bates *et al.*, 1995], which compromised the CH<sub>4</sub> precision to approximately ±2% based on the average percent standard deviation of the standard response over a 6-hour period.

All mixing ratios are reported here in units of parts per billion (10<sup>9</sup>) by volume (ppb) in dry air and are based on the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) scale [Dlugokencky *et al.*, 1994b]. The calibration history of the CMDL CH<sub>4</sub> primary standards are discussed by Dlugokencky *et al.* [1994b]. The PMEL CH<sub>4</sub> standards in the range of 1617 to 1767 ppb were dried, whole air mixtures contained in aluminum cylinders. Three cylinders were initially filled and calibrated for CH<sub>4</sub> by CMDL in 1987. Standards at 1591 and 2024 ppb were synthetic mixtures prepared by specialty gas companies. The original three cylinders, along with four additional cylinders, were recalibrated by CMDL in 1991. No significant drift was observed in the three original cylinders or in subsequent intercalibrations of the seven cylinders.

#### Data Reduction

The data were filtered visually to eliminate episodes of atmospheric contamination from the ship. These episodes were indicated by extremely high CO values (greater than 10 times ambient) that occurred when the ship was running downwind.

Data also were filtered to eliminate periods when the ship was stopped on station, since discharges from the ship can be a source of seawater CH<sub>4</sub> contamination, especially on older ships that do not have a sewage system holding tank. Seawater data from SAGA 1987 were eliminated, since the water inlet was aft of some overboard discharges and the data set contained occasional erratically high concentrations. Seawater data from the northbound leg of RITS 1989 were eliminated due to an equilibrator malfunction.

CH<sub>4</sub> dry-air mixing ratios in both air ((X)<sub>a</sub>) and equilibrator headspace ((X)<sub>e</sub>) samples were computed from peak height and a 6-hour running-mean single-point standard. The data then were binned into hourly intervals and smoothed using an 8-point Lowess filter-fitted program based on a least squares method [Cleveland *et al.*, 1988]. Gas solubilities in mmol l<sup>-1</sup> atm<sup>-1</sup> were calculated for each hourly CH<sub>4</sub> value at both the local surface seawater temperature (SST) and equilibrator temperature using the local seawater salinity and the equilibrium solubility equations of Wiesenburg and Guinasso [1979]. CH<sub>4</sub> mixing ratios measured in the equilibrator headspace ((X)<sub>e</sub>) were corrected to SST ((X)<sub>w</sub>) using the ratio of the gas solubilities at the two temperatures. This correction reduced ((X)<sub>e</sub>) by approximately 0.59% for an average warming of 0.26°C.

The temperature-corrected, dry CH<sub>4</sub> mixing ratios were used to calculate ΔpCH<sub>4</sub> in units of micro atmospheres,

$$\Delta p\text{CH}_4 = (P_a - P_w) [(X)_w - (X)_a] \quad (1)$$

where ΔpCH<sub>4</sub> is the difference in the air and seawater partial

pressures of  $\text{CH}_4$ ,  $P_a$  is the atmospheric pressure, and  $P_w$  is the saturation water vapor pressure calculated at the local sea surface temperature and salinity according to *Weiss and Price* [1980]. The nM concentration of  $\text{CH}_4$  in surface seawater was calculated as the product of the gas solubility and the seawater  $\text{CH}_4$  partial pressure.

## Results and Discussion

### Atmospheric $\text{CH}_4$ Mixing Ratios

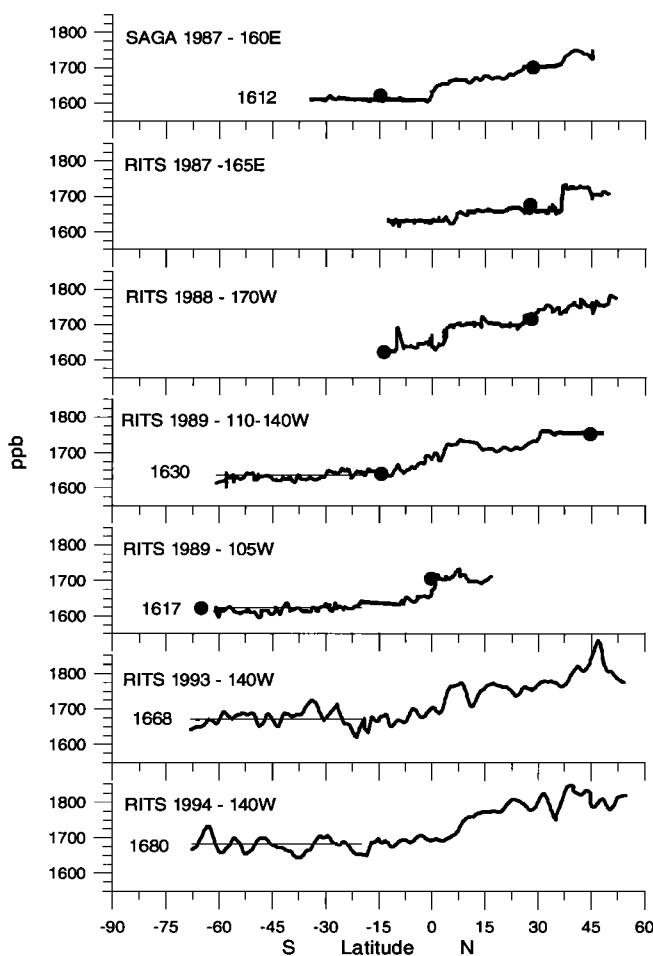
Latitudinal distributions of tropospheric  $\text{CH}_4$  can provide a constraint on model calculations of sources and sinks [*Fung et al.*, 1991]. Measurements from globally distributed networks yield latitudinal distributions as well as seasonal cycles and long-term trends [*Steele et al.*, 1987; *Dlugokencky et al.*, 1994b]. Shipboard measurements can provide a more detailed snapshot of latitudinal distributions.

Atmospheric  $\text{CH}_4$  mixing ratios measured during this study ranged from 1590 to 1890 ppb and were consistent with the NOAA/CMDL [*Dlugokencky et al.*, 1994b] baseline station data at Palmer Station, American Samoa, Midway, and Cape Meares (Figure 2) within the uncertainty of the measurements. The data show a pronounced interhemispheric gradient. Synoptic-scale variations from the mean hemispheric concentrations probably are related to mixing from the free troposphere [*Matsueda et al.*, 1993] or long-range transport [*Khalil et al.*, 1993]. Although the cruise tracks were purposely chosen with little overlap in time and space in order to assess the regional and seasonal variations in atmospheric and seawater  $\text{CH}_4$  partial pressures, the general trend of increasing atmospheric  $\text{CH}_4$  mixing ratios with respect to time is evident in the data. The average southern hemisphere ( $20^\circ$ – $70^\circ\text{S}$ )  $\text{CH}_4$  mixing ratio was 1612 ppb in May–June 1987, increasing to 1630 ppb in March–April 1989 and 1668 ppb in April 1993. While it is difficult to quantify accurately inter-annual trends in the atmospheric levels of  $\text{CH}_4$  from these data due to seasonal variations, the general trend of increasing concentrations is consistent with that of *Dlugokencky et al.* [1994a].

### Seawater $\text{CH}_4$ Concentrations and Saturation Ratios

Surface seawater  $\text{CH}_4$  concentrations throughout the open Pacific Ocean ranged from 1.6 to 3.6 nM and were very close to saturation equilibrium values (Figure 3). Saturation ratios (SR), which are the ratio of the measured mixing ratios in air equilibrated with seawater to the measured mixing ratios in the overlying atmosphere [ $(X)_w/(X)_a$ ], are useful in indicating deviations from equilibrium. Open Pacific Ocean SR ranged from 0.95 to 1.17 (Figure 4) and were always positive in the region between  $5^\circ\text{N}$  and  $30^\circ\text{S}$ . Poleward of this region, the SR varied seasonally with large regions of undersaturation in the fall and winter.

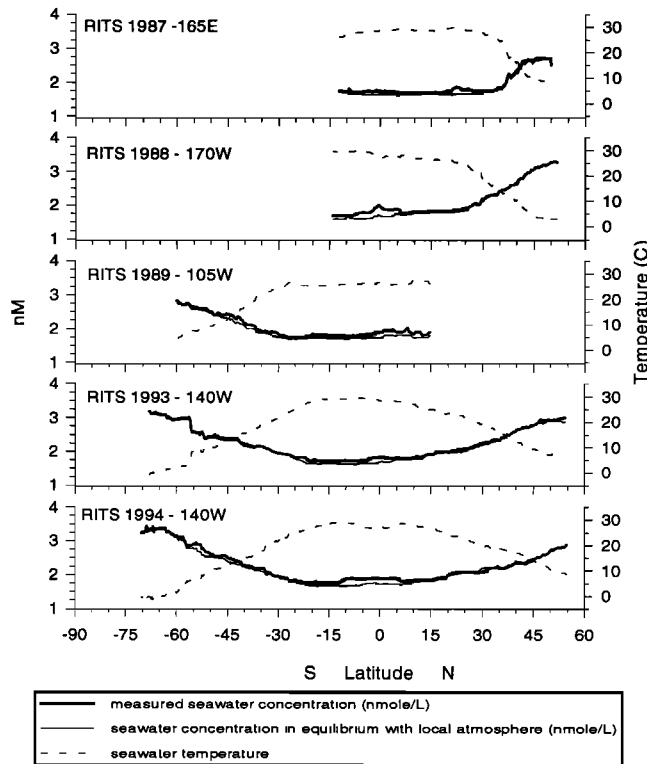
There are several factors which potentially could affect the magnitude and sign of the SR. The approximately  $11 \text{ ppb yr}^{-1}$  globally averaged (1983–1992) increase in the atmospheric  $\text{CH}_4$  mixing ratio [*Dlugokencky et al.*, 1994b] would lead to a decrease in the SR if all other factors remained constant. The cruises in 1988 and 1993 crossed the North Pacific during the month of April and thus provide an opportunity to compare interannual differences. The North Pacific ( $15^\circ\text{N}$ – $50^\circ\text{N}$ ) SR calculated for these cruises were  $1.008 \pm 0.011$  and  $1.009 \pm 0.016$  in 1988 and 1993, respectively. Therefore, although the atmospheric  $\text{CH}_4$  mixing ratios increased, the ocean was in the same state of near-equilibrium in 1988 and 1993.



**Figure 2.** Atmospheric  $\text{CH}_4$  mixing ratios in ppb along the meridional cruise tracks. The solid circles are data from NOAA/CMDL at Palmer Station, Antarctica ( $64^\circ 55'\text{S}$ ,  $64^\circ 00'\text{W}$ ); Tutuila, American Samoa ( $14^\circ 15'\text{S}$ ,  $170^\circ 34'\text{W}$ ); Sand Island, Midway ( $28^\circ 13'\text{N}$ ,  $177^\circ 22'\text{W}$ ); and Cape Meares, Oregon ( $45^\circ 29'\text{N}$ ,  $123^\circ 58'\text{W}$ ) [*Dlugokencky et al.*, 1994b]. The thin lines are the average mixing ratios measured in the southern hemisphere from  $20^\circ$  to  $70^\circ\text{S}$ .

SR also are influenced by the seasonal change in atmospheric  $\text{CH}_4$  mixing ratios, which are highest in winter due to a combination of enhanced sources, diminished sinks and transport [*Dlugokencky et al.*, 1994b]. The globally averaged seasonal amplitude in atmospheric  $\text{CH}_4$  mixing ratios is approximately 30 ppb, although there is a high frequency variability on synoptic timescales [*Dlugokencky et al.*, 1994b]. This seasonal cycle would affect the SR by approximately 0.3% per month.

Higher wind speeds enhance air-sea exchange, which will tend to drive the SR toward a value of 1. Since the net flux is driven by the difference in  $\text{CH}_4$  atmospheric and seawater partial pressures, the magnitude of the flux will decrease as the SR approaches 1. Assuming an average flux of  $0.2 \mu\text{mol m}^{-2} \text{d}^{-1}$  at a wind speed of  $6.9 \text{ m s}^{-1}$  (see below), an average seawater  $\text{CH}_4$  concentration of 2.6 nM, and a 100-m upper ocean mixed depth, air-sea exchange could reduce the SR by approximately 2% per month. The magnitude of this change is within the regional variability observed in the SR (Figure 4). Furthermore, there was no observed anticorrelation between the wind speed measured aboard ship and  $\Delta p\text{CH}_4$ . *Conrad and Seiler* [1988] noted a

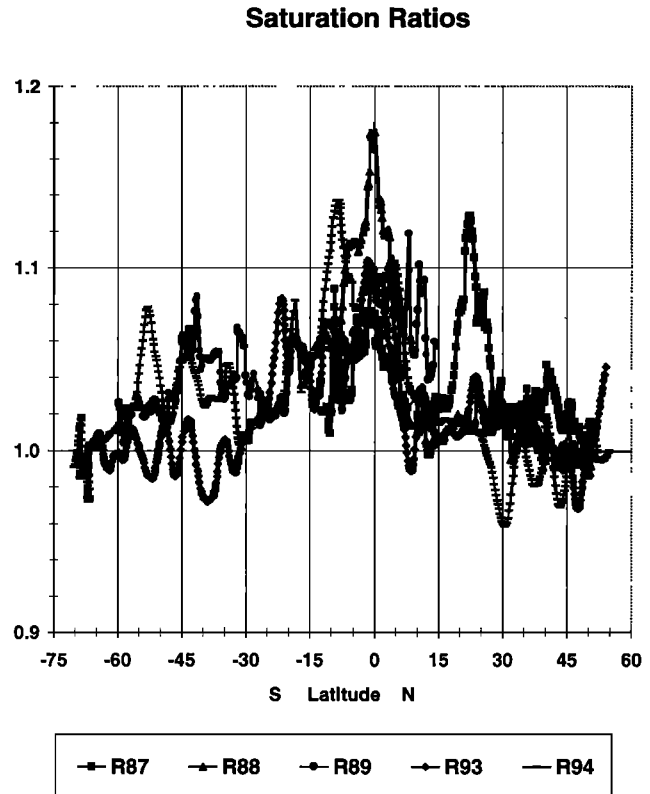


**Figure 3.** Measured surface seawater  $\text{CH}_4$  concentrations in  $\text{nmol L}^{-1}$  (thick lines), seawater concentrations that would be in equilibrium with the local atmospheric  $\text{CH}_4$  concentrations (thin line), and SST (dashed line) along the meridional cruise tracks.

similar lack of correlation between SR and wind speed in their  $\text{CH}_4$  measurements from the Atlantic Ocean.

There also are several oceanographic factors which could affect the SR. Since  $\text{CH}_4$  is produced in the digestive tracts of zooplankton [de Angelis and Lee, 1994],  $\text{CH}_4$  production rates in the water column should be a function of zooplankton grazing rates. Although zooplankton were not directly measured on these cruises, there was no observed correlation of  $\text{CH}_4$  concentrations with surface seawater chlorophyll fluorescence (phytoplankton biomass) or nitrate. The general lack of correlation between surface seawater  $\text{CH}_4$  concentrations and seawater biological/chemical parameters observed here and in numerous other studies [Burke *et al.*, 1983; Conrad and Seiler, 1988; Tilbrook and Karl, 1994] suggests that the timescales of biological  $\text{CH}_4$  production processes must be short compared with that of physical mixing.

Physical circulation processes within the ocean could affect the SR, since maximum water column  $\text{CH}_4$  concentrations often are found near the pycnocline [Burke *et al.*, 1983]. The higher SR in the equatorial region of the Pacific Ocean could be a result of the upwelling of colder water with high SR. As this upwelled water moves away from the equator, its SR is enhanced by warming and reduced by air-sea exchange. The average SR from all cruises was  $1.085 \pm 0.035$  from  $5^\circ\text{N}$  to  $5^\circ\text{S}$ , as opposed to  $1.021 \pm 0.027$  for the regions poleward of  $5^\circ$ . The highest SR were measured in 1988, which was during a La Niña period of negative SST anomalies (Tropical Atmosphere/Ocean (TAO) project office/PMEL/NOAA), indicative of stronger than normal upwelling. The lowest equatorial SR were measured in 1987 during a strong El Niño when equatorial upwelling had ceased.



**Figure 4.**  $\text{CH}_4$  saturation ratios along the meridional cruise tracks.

Conrad and Seiler [1988] observed similar increases in  $\text{CH}_4$  SR in upwelling areas of the Atlantic Ocean.

Finally, SR will change with the seasonal change in SST. From  $15^\circ$  to  $60^\circ\text{N}$  and S, SST changes approximately  $0.9^\circ\text{C}$  per month. This causes an average 2% change in  $\text{CH}_4$  solubility and a corresponding 2% change in SR per month. The net effect is undersaturated surface water in the fall and supersaturated surface water in the spring. Although there is a paucity of fall and winter  $\text{CH}_4$  measurements in the literature, previous measurements by Conrad and Seiler [1988] in the North Atlantic and Tilbrook and Karl [1995] in the Drake Passage showed below-average saturation ratios during the fall.

In summary, equatorial upwelling and seasonal changes in SST appear to be the dominant factors controlling the  $\text{CH}_4$  SR in tropical and extratropical regions, respectively. Based on this analysis and the latitudinal and seasonal features in the surface seawater  $\text{CH}_4$  SR measured between 1988 and 1994 (Figure 4), the  $\text{CH}_4$  data from the PMEL meridional cruise tracks (Figure 1) were averaged into ten  $15^\circ$  zonal regions and two seasons (Table 2). The  $15^\circ$  zones were chosen to bound the major oceanographic features of the Pacific (equatorial upwelling region, gyres, subtropical and sub-Antarctic convergences) and were found to be a better indicator of  $\text{CH}_4$  concentrations in the Pacific than chlorophyll or other biogeographical parameterizations. The seasons were chosen as periods of cooling (fall-winter) and warming (spring-summer) to reflect the seasonal changes in SST. Blank values in Table 2 indicate regions without data. Based on the 95% confidence interval for the mean in each latitude zone, the estimated uncertainty in the seasonally and zonally averaged SR is  $\pm 2\%$ .

**Table 2.** Regional and Seasonal Seawater CH<sub>4</sub> Saturation Ratio, Seawater/Atmospheric CH<sub>4</sub> Partial Pressure Differences, Seawater Temperature, Wind Speeds, CH<sub>4</sub> Solubilities, and Transfer Velocities

Region	Cruise Number (see Table 1)	CH <sub>4</sub> , SR	$\Delta p\text{CH}_4$ , $\mu\text{atm}$	SST, $^{\circ}\text{C}$	Solubility, $\text{mmol L}^{-1}$ $\text{atm}^{-1}$	Wind Speed, $\text{m s}^{-1}$	Transfer Velocity ( $k_t$ ), $\text{m d}^{-1}$
<i>March–August</i>							
60°–75°S	7	1.00	–0.001	0.3	1.97	7.6	3.1
45°–60°S	7	1.00	–0.002	5.5	1.70	9.0	5.0
30°–45°S	7	0.99	–0.010	15.8	1.33	7.7	5.0
15°–30°S	7	1.05	0.079	23.5	1.14	6.4	4.2
0°–15°S	2,3,7	1.07	0.104	27.1	1.06	5.7	3.6
0°–15°N	2,3,7	1.04	0.063	27.9	1.05	5.8	3.7
15°–30°N	2,3,7	1.03	0.052	25.2	1.10	6.3	4.1
30°–45°N	2,3,7	1.01	0.020	17.5	1.28	6.9	4.1
45°–60°N	2,3,7	1.00	0.005	8.1	1.59	7.6	3.9
60°–75°N	—	—	0.005	3.9	1.78	6.4	2.4
<i>September–February</i>							
60°–75°S	8	1.00	0.005	–0.2	2.00	6.7	2.3
45°–60°S	4,8	1.03	0.046	5.4	1.71	8.9	4.9
30°–45°S	4,8	1.04	0.067	16.0	1.33	7.1	4.2
15°–30°S	4,8	1.03	0.043	23.5	1.14	6.2	3.9
0°–15°S	4,8	1.07	0.111	26.7	1.07	5.4	3.2
0°–15°N	4,8	1.06	0.106	27.5	1.05	5.8	3.7
15°–30°N	8	1.00	0.008	25.1	1.10	6.7	4.6
30°–45°N	8	0.99	–0.013	17.4	1.29	8.5	6.2
45°–60°N	8	1.00	0.001	7.7	1.61	10.0	6.6
60°–75°N	—	—	0.001	3.7	1.45	8.3	4.1

SST/wind speed from the Comprehensive Ocean-Atmosphere Data Set (COADS); solubilities from *Wiesenburg and Guinasso* [1979]; transfer velocities calculated from *Wanninkhof* [1992].

The CH<sub>4</sub> SR measured here are within the range of values measured in the Atlantic by *Conrad and Seiler* [1988] and those summarized by *Bange et al.* [1994] and *Tilbrook and Karl* [1995] for the world's oceans. Early measurements (late 1960s and early 1970s) in the Pacific by *Lamontagne et al.* [1971, 1973, 1974] suggested that the ocean was much more supersaturated at that time with average SR of approximately 1.3. The data reported here from the North Pacific in 1988 and 1993 suggest that the SR has not changed with increasing atmospheric CH<sub>4</sub> mixing ratios. Assuming sound sampling and analysis techniques, the data suggest that the open ocean CH<sub>4</sub> source may have decreased in the past two decades. Whether this could be due to a decrease in macrozooplankton biomass [*Roemmich and McGowan*, 1995] or some other ecological factor is an open question. Recent measurements in the western Pacific by *Watanabe et al.* [1995] showed a SR of  $31 \pm 4\%$ , which is consistent with the earlier data of *Lamontagne* and coworkers. Unfortunately, it is not possible to resolve these differences with the available data.

#### CH<sub>4</sub> Air-Sea Exchange

The ocean-atmosphere flux ( $F$ ) of CH<sub>4</sub> can be expressed as

$$F = K_t L \Delta p\text{CH}_4 \quad (2)$$

where  $K_t$  is the gas transfer velocity expressed in units of length/time,  $L$  is the gas solubility at the ambient surface seawater temperature expressed in units of concentration/pressure, and  $\Delta p\text{CH}_4$  is the CH<sub>4</sub> partial pressure difference between surface seawater and the overlying atmosphere.  $K_t$  can

be parameterized using wind speed and Schmidt number, which is the ratio of kinematic viscosity of seawater to the molecular diffusivity of the gas [*Liss and Merlivat*, 1986; *Wanninkhof*, 1992].

The relationship between wind speed and gas exchange over the ocean can be parameterized in several ways, resulting in a difference in the calculated gas fluxes of approximately a factor of 2 [*Wanninkhof*, 1992]. The choice of wind speed/transfer velocity relationships and wind fields depends on the objectives of the study [*Murphy et al.*, 1991; *Wanninkhof*, 1992; *Liss et al.*, 1993]. Transfer velocities calculated using shipboard winds will provide the best estimate of the instantaneous flux and are an important consideration if the local wind speed significantly affects the SR. However, based on the analysis presented above, an average ocean-atmosphere CH<sub>4</sub> flux affects the CH<sub>4</sub> SR only by 2% month<sup>–1</sup>. In addition, there was no observed anti-correlation between wind speed and CH<sub>4</sub> SR from any of the cruises. Consequently, since the main purpose of this study was to estimate regional and seasonal ocean-atmosphere CH<sub>4</sub> fluxes rather than instantaneous fluxes, we have chosen to use seasonal ocean wind speeds and SST from the 40-year climatological Comprehensive Ocean-Atmosphere Data Set (COADS) [*Woodruff et al.*, 1987] together with a transfer velocity relationship for long-term averaged winds [*Wanninkhof*, 1992].

Hourly CH<sub>4</sub> partial pressures were used to calculate hourly  $\Delta p\text{CH}_4$  values from the five cruises (equation (1)). The data from each cruise then were binned into zonal means. The zonal  $\Delta p\text{CH}_4$  values and the monthly  $2^{\circ} \times 2^{\circ}$  COADS SST and wind speed ( $u$  in  $\text{m s}^{-1}$ ) data were averaged zonally and seasonally (Table 2). COADS SSTs were used to calculate gas solubilities [*Wiesenburg and Guinasso*, 1979] and diffusivities [*Jahne et al.*,

1987]. Gas diffusivities in freshwater were reduced by 6% to correct for the ionic strength of seawater [Jahne *et al.*, 1987] and then used to calculate a Schmidt number ( $Sc$ ) (680 at 20°C and salinity of 35 ppt) for each region and season. Finally, the regional and seasonal  $CH_4$  transfer velocities in  $cm\ hr^{-1}$  were calculated according to Wanninkhof [1992], where

$$K_t = 0.39 u^2 (Sc/660)^{-0.5}. \quad (3)$$

Transfer velocities from equation (3), solubilities, and  $\Delta pCH_4$  values (Table 2) were used to calculate the regional and seasonal fluxes using equation (2). Fluxes range from a winter low in the high latitudes of  $-0.1\ \mu mol\ m^{-2}\ d^{-1}$  to an equatorial high of  $0.4\ \mu mol\ m^{-2}\ d^{-1}$ . The average global flux is  $0.15\ \mu mol\ m^{-2}\ d^{-1}$ . Regional annual  $CH_4$  emissions (the product of the flux and regional area) range from 0 to  $7.1\ Gmol\ yr^{-1}$  with 2/3 of the emissions in the southern hemisphere. The total annual ocean  $CH_4$  emission is  $25\ Gmol$  (Table 3). This value is an order of magnitude less than previous calculations; however, this estimate is the first to take into account seasonally and zonally averaged measured  $CH_4$  seawater partial pressures. The major uncertainties in this emission estimate include the regionally and seasonally averaged  $CH_4$  seawater and atmospheric partial pressures ( $\pm 2\%$ ), the wind fields used for calculating transfer velocities ( $\pm 30\%$ ) [Murphy *et al.*, 1991; Wanninkhof, 1992], and the choice of the wind speed/transfer velocity relationship ( $\pm 50\%$ , Table 4).

For comparison,  $CH_4$  transfer velocities, fluxes, and emissions were calculated for the hourly data using shipboard winds and the transfer velocity/wind speed relationship of both Liss and Merlivat [1986] and Wanninkhof [1992]. The shipboard winds during these cruises were on average 30% higher than the 40-year climatological COADS winds (Table 4). The average transfer velocity calculated using shipboard winds and the Wanninkhof [1992] short-term wind speed/transfer velocity relationship was 50% higher than the average transfer velocity calculated using COADS winds and the Wanninkhof [1992] long-term wind speed/transfer velocity relationship. Finally, the average transfer velocity calculated using shipboard winds and the Liss and Merlivat [1986] wind speed/transfer velocity relationship was 15% lower than the average transfer velocity

calculated using COADS winds and the Wanninkhof [1992] long-term wind speed/transfer velocity relationship (Table 4). The emissions calculated from these two wind fields and two transfer velocity relationships thus range from 13 to  $38\ Gmol\ yr^{-1}$ .

## Conclusions

$CH_4$  mixing ratios in the marine boundary layer measured during this series of cruises showed synoptic variability, a latitudinal gradient, and a general increase with time, consistent with data from NOAA's globally distributed network of sites [Dlugokencky *et al.*, 1994b]. The partial pressure of  $CH_4$  in seawater varied regionally and seasonally and increased from 1988 to 1993. During this time, the  $CH_4$  saturation ratio in the North Pacific Ocean during April appears to have remained constant. Although anthropogenic emissions have perturbed the background atmospheric  $CH_4$  burden, the ocean adjusts to this increase and continues to be a small source of  $CH_4$  to the atmosphere in this region during April. These results are consistent with the general understanding of the marine  $CH_4$  cycle: a small  $CH_4$  source in the water column balanced primarily by an air-sea exchange sink. If this ocean source remains constant, the surface ocean  $CH_4$  partial pressure will continue to track the atmospheric concentration, and the SR will always be on average slightly greater than 1, consistent with the model of Bange *et al.* [1994].

Open Pacific Ocean saturation ratios measured during this series of cruises ranged from 0.95 to 1.17. Large areas of the Pacific Ocean were undersaturated with respect to atmospheric  $CH_4$  partial pressures during the fall and winter. On a seasonal timescale, the driving force controlling the SR outside the tropics appeared to be the change in sea surface temperature. Saturation ratios in the equatorial region were always positive and appeared to be driven by the strength of the equatorial upwelling. Although these data cover only the Pacific Ocean, the values obtained are similar to those recently reported in the Atlantic. Extrapolating our data globally and dividing the open ocean seasonally into two periods and regionally into 10 zones, the calculated average flux of  $CH_4$  to the atmosphere was  $25\ Gmol\ yr^{-1}$  (13 to  $38\ Gmol\ yr^{-1}$ ). This is approximately an

**Table 3.** Regional and Seasonal Emissions of  $CH_4$  From the Ocean to the Atmosphere in gigamoles per season or year

Region	Area, $10^6\ km^2$	Season		Annual
		mamjja	sondjf	
60°–75°S	19.3	–0.02	0.08	0.1
45°–60°S	39.0	–0.12	2.76	2.6
30°–45°S	46.8	–0.57	3.20	2.6
15°–30°S	46.1	3.20	1.60	4.8
0°–15°S	49.8	3.62	3.49	7.1
0°–15°N	49.5	2.24	3.73	6.0
15°–30°N	39.0	1.72	0.29	2.0
30°–45°N	27.9	0.53	–0.54	0.0
45°–60°N	16.6	0.09	0.03	0.1
60°–75°N	8.5	0.03	0.01	0.0
Southern Hemisphere	200	6.1	11.1	17.2
Northern Hemisphere	140	4.6	3.5	8.1
Total	340	10.7	14.6	25.3

Fluxes calculated using transfer velocities from Wanninkhof [1992], regional area from Levitus [1982]. Seasons are mamjja (March, April, May, June, July, August) and sondjf (September, October, November, December, January, February).

**Table 4.** Area-Weighted Annual Average Wind Speeds, Transfer Velocities, and CH<sub>4</sub> Fluxes and Emissions From the Five Meridional Cruises

Wind Field	COADS	Ship
Wind speed, m s <sup>-1</sup>	6.9 <sup>a</sup>	9.0
<i>K<sub>p</sub></i> , m d <sup>-1</sup>		
<i>Liss and Merlivat</i> [1986]	2.1	3.7
<i>Wanninkhof</i> [1992]	4.2	6.7
Flux, μmol m <sup>-2</sup> d <sup>-1</sup>		
<i>Liss and Merlivat</i> [1986]	0.10	0.17
<i>Wanninkhof</i> [1992]	0.20 <sup>b</sup>	0.30 <sup>c</sup>
Emissions, Gmol yr <sup>-1</sup>		
<i>Liss and Merlivat</i> [1986]	13	21
<i>Wanninkhof</i> [1992]	25	38

<sup>a</sup>Seasonally and zonally averaged data.

<sup>b</sup>Calculated using the *Wanninkhof* [1992] long-term wind speed proportionality factor (0.39).

<sup>c</sup>Calculated using the *Wanninkhof* [1992] short-term wind speed proportionality factor (0.31).

order of magnitude less than previous estimates, which lacked fall and winter data.

Clearly, the open ocean is a very minor source of methane to the atmosphere (<0.1%) compared with other sources [IPCC, 1994]. However, the coastal ocean and marginal seas appear to be a much larger source [Owens *et al.*, 1991; Kvenvolden *et al.*, 1993; Bange *et al.*, 1994; Lammers *et al.*, 1995] due to CH<sub>4</sub> emissions from bottom sediments, and definitely warrant further investigation.

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## References

- Bange, H. W., U. H. Bartell, S. Rapsomanikis, and M. O. Andreae, Methane in the Baltic and North Seas and a reassessment of the marine emission of methane, *Global Biogeochem. Cycles*, **8**, 465–480, 1994.
- Bates, T. S., K. C. Kelly, and J. E. Johnson, Concentrations and fluxes of dissolved biogenic gases (DMS, CH<sub>4</sub>, CO, CO<sub>2</sub>) in the equatorial Pacific during the SAGA 3 experiment, *J. Geophys. Res.*, **98**, 16,969–16,978, 1993.
- Bates, T. S., K. C. Kelly, J. E. Johnson, and R. H. Gammon, Regional and seasonal variations in the flux of oceanic carbon monoxide to the atmosphere, *J. Geophys. Res.*, **100**, 23,093–23,101, 1995.
- Bianchi, M., D. Marty, J.-L. Teyssie, and S. W. Fowler, Strictly aerobic and anaerobic bacteria associated with sinking particulate matter and zooplankton fecal pellets, *Mar. Ecol. Prog. Ser.*, **88**, 55–60, 1992.
- Blake, D. R., and F. S. Rowland, Continuing worldwide increase in tropospheric methane, 1978 to 1987, *Science*, **239**, 1129–1131, 1988.
- Burke, R. A., Jr., D. F. Reid, J. M. Brooks, and D. M. Lavoie, Upper water column methane geochemistry in the eastern tropical North Pacific, *Limnol. Oceanogr.*, **28**, 19–32, 1983.
- Butler, J. H., J. W. Elkins, C. M. Brunson, K. B. Egan, T. M. Thompson, T. J. Conway, and B. D. Hall, Trace gases in and over the West Pacific and East Indian Oceans during the El Niño-Southern Oscillation event of 1987, *NOAA Data Rep., ERL ARL-16*, 104 pp., Air Resour. Lab., Silver Spring, Md., 1988.
- Chappellaz, J., T. Blunier, D. Raynaud, J. M. Barnola, J. Schwander, and B. Stauffer, Synchronous changes in atmospheric CH<sub>4</sub> and Greenland climate between 40 and 8 kyr BP, *Nature*, **366**, 443–445, 1993.
- Cicerone, R. J., and R. S. Oremland, Biogeochemical aspects of atmospheric methane, *Global Biogeochem. Cycles*, **2**, 299–328, 1988.
- Cleveland, W. S., S. J. Devlin, and E. Grosse, Regression by local fitting, *J. Econometrics*, **37**, 87–114, 1988.
- Conrad, R., and W. Seiler, Methane and hydrogen in seawater (Atlantic Ocean), *Deep Sea Res.*, **35**, 1903–1917, 1988.
- Crutzen, P. J., and P. H. Zimmerman, The changing photochemistry of the troposphere, *Tellus*, **43AB**, 136–151, 1991.
- de Angelis, M. A., and C. Lee, Methane production during zooplankton grazing on marine phytoplankton, *Limnol. Oceanogr.*, **39**, 1298–1308, 1994.
- Dlugokencky, E. J., K. A. Masarie, P. M. Lang, P. P. Tans, L. P. Steele, and E. G. Nisbet, A dramatic decrease in the growth rate of atmospheric methane in the northern hemisphere during 1992, *Geophys. Res. Lett.*, **21**, 45–48, 1994a.
- Dlugokencky, E. J., L. P. Steele, P. M. Lang, and K. A. Masarie, The growth rate and distribution of atmospheric methane, *J. Geophys. Res.*, **99**, 17,021–17,043, 1994b.
- Ehhalt, D. H., The atmospheric cycle of methane, *Tellus*, **26**, 58–70, 1974.
- Etheridge, D. M., G. I. Pearman, and P. J. Fraser, Changes in tropospheric methane between 1841 and 1978 from a high accumulation-rate Antarctic ice core, *Tellus*, **44B**, 282–294, 1992.
- Fung, I., J. John, J. Lerner, E. Matthews, M. Prather, L. P. Steele, and P. J. Fraser, Three-dimensional model synthesis of the global methane cycle, *J. Geophys. Res.*, **96**, 13,033–13,065, 1991.
- Intergovernmental Panel on Climate Change (IPCC), *Radiative Forcing of Climate Change*, edited by J. T. Houghton *et al.*, 339 pp., Cambridge Univ. Press, New York, 1994.
- Jahne, B., G. Heinz, and W. Dietrich, Measurements of the diffusion coefficients of sparingly soluble gases in water, *J. Geophys. Res.*, **92**, 10,767–10,776, 1987.
- Jones, R. D., Carbon monoxide and methane distribution and consumption in the photic zone of the Sargasso Sea, *Deep Sea Res.*, **38**, 625–635, 1991.
- Karl, D. M., and B. D. Tilbrook, Production and transport of methane in oceanic particulate organic matter, *Nature*, **368**, 732–734, 1994.
- Khalil, M. A. K., R. A. Rasmussen, and F. Moraes, Atmospheric methane at Cape Meares: Analysis of a high-resolution data base and its environmental implications, *J. Geophys. Res.*, **98**, 14,753–14,770, 1993.
- Kiene, R. P., Production and consumption of methane in aquatic systems, in *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides and Halomethanes*, edited by J. E. Rogers and W. B. Whitman, pp. 111–146, Am. Soc. of Microbiol., Washington, D.C., 1991.
- Kvenvolden, K. A., M. D. Lilley, T. D. Lorenson, P. W. Barnes, and E. McLaughlin, The Beaufort Sea continental shelf as a



- seasonal source of atmospheric methane, *Geophys. Res. Lett.*, **20**, 2459–2462, 1993.
- Lambert, G., and S. Schmidt, Reevaluation of the oceanic flux of methane: Uncertainties and long-term variations, *Chemosphere*, **26**, 579–589, 1993.
- Lammers, S., E. Suess, M. N. Mansurov, and V. V. Anikey, Variations of atmospheric methane supply from the Sea of Okhotsk induced by the seasonal ice cover, *Global Biogeochem. Cycles*, **9**, 351–358, 1995.
- Lamontagne, R. A., J. W. Swinnerton, and V. J. Linnenbom, Nonequilibrium of carbon monoxide and methane at the air-sea interface, *J. Geophys. Res.*, **76**, 5117–5121, 1971.
- Lamontagne, R. A., J. W. Swinnerton, V. J. Linnenbom, and W. D. Smith, Methane concentrations in various marine environments, *J. Geophys. Res.*, **78**, 5317–5324, 1973.
- Lamontagne, R. A., J. W. Swinnerton, and V. J. Linnenbom, C<sub>1</sub>-C<sub>4</sub> hydrocarbons in the North and South Pacific, *Tellus*, **26**, 71–77, 1974.
- Levitus, S., Climatological atlas of the world ocean, *NOAA Prof. Pap.*, **13**, 173 pp., 1982.
- Liss, P. S., and L. Merlivat, Air-sea gas exchange rates: Introduction and synthesis, in *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Buat-Menard, pp. 113–127, D. Reidel, Norwell, Mass., 1986.
- Liss, P. S., A. J. Watson, M. I. Liddicoat, G. Malin, P. D. Nightingale, S. M. Turner, and R. C. Upstill-Goddard, Trace gases and air-sea exchanges, *Philos. Trans. R. Soc. London A*, **343**, 531–541, 1993.
- Marty, D. G., Methanogenic bacteria in seawater, *Limnol. Oceanogr.*, **38**, 452–456, 1993.
- Matsueda, H., H. Inoue, and M. Ishii, Latitudinal distributions of methane in the upper troposphere and marine boundary air over the Pacific in 1990, *Geophys. Res. Lett.*, **20**, 695–698, 1993.
- Murphy, P. P., R. A. Feely, R. H. Gammon, D. E. Harrison, K. C. Kelly, and L. S. Waterman, Assessment of the air-sea exchange of CO<sub>2</sub> in the South Pacific during austral autumn, *J. Geophys. Res.*, **96**, 20,455–20,465, 1991.
- Murphy, P. P., C. Cosca, D. C. Lee, and R. A. Feely, Temperature calibration and correction report for PMEL trace gas cruises 1986–1989, *NOAA Tech. Memo., ERL PMEL-97*, 192 pp., 1993.
- Owens, N. J. P., C. S. Law, R. F. C. Mantoura, P. H. Burkill, and C. A. Llewellyn, Methane flux to the atmosphere from the Arabian Sea, *Nature*, **354**, 293–296, 1991.
- Rasmussen, R. A., and M. A. K. Khalil, Atmospheric methane in the recent and ancient atmospheres: Concentrations, trends, and interhemispheric gradient, *J. Geophys. Res.*, **89**, 11,599–11,605, 1984.
- Roemmich, D., and J. McGowan, Climatic warming and the decline of zooplankton in the California current, *Science*, **267**, 1324–1326, 1995.
- Scranton, M. I., and P. G. Brewer, Occurrence of methane in the near-surface waters of the western subtropical North Atlantic, *Deep Sea Res.*, **24**, 127–138, 1977.
- Steele, L. P., P. J. Fraser, R. A. Rasmussen, M. A. K. Khalil, T. J. Conway, A. J. Crawford, R. H. Gammon, K. A. Masarie, and K. W. Thoning, The global distribution of methane in the troposphere, *J. Atmos. Chem.*, **5**, 125–171, 1987.
- Steele, L. P., E. J. Dlugokencky, P. M. Lang, P. P. Tans, R. C. Martin, and K. A. Masarie, Slowing down of the global accumulation of atmospheric methane during the 1980s, *Nature*, **358**, 313–316, 1992.
- Tilbrook, B. D., and D. M. Karl, Dissolved methane distributions, sources and sinks in the western Bransfield Strait, Antarctica, *J. Geophys. Res.*, **99**, 16,383–16,393, 1994.
- Tilbrook, B. D., and D. M. Karl, Methane sources, distributions and sinks from California coastal waters to the oligotrophic North Pacific gyre, *Mar. Chem.*, **49**, 51–64, 1995.
- Traganza, E. D., J. W. Swinnerton, and C. H. Cheek, Methane supersaturation and ATP-zooplankton blooms in near-surface waters of the western Mediterranean and the subtropical North Atlantic Ocean, *Deep Sea Res.*, **26A**, 1237–1245, 1979.
- Wanninkhof, R. H., Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, **97**, 7373–7382, 1992.
- Ward, B. B., K. A. Kilpatrick, P. C. Novelli, and M. I. Scranton, Methane oxidation and methane fluxes in the ocean surface layer and deep anoxic waters, *Nature*, **327**, 226–229, 1987.
- Watanabe, S., N. Higashitani, N. Tsurushima, and S. Tsunogai, Methane in the western North Pacific, *J. Ocean.*, **51**, 39–60, 1995.
- Weiss, R. F., Determinations of carbon dioxide and methane by dual catalyst flame ionization chromatography and nitrous oxide by electron capture chromatography, *J. Chromatogr.*, **19**, 611–616, 1981.
- Weiss, R. F., and B. A. Price, Nitrous oxide solubility in water and seawater, *Mar. Chem.*, **8**, 347–359, 1980.
- Wiesenburg, D. A., and N. L. Guinasso Jr., Equilibrium solubilities of methane, carbon monoxide and hydrogen in water and seawater, *J. Chem. Eng. Data*, **24**, 356–360, 1979.
- Woodruff, S. D., R. J. Slutz, R. L. Jene, and M. Steurer, A comprehensive ocean-atmosphere data set, *Bull. Am. Meteorol. Soc.*, **68**, 1239–1250, 1987.
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