

Regional and seasonal variations in the flux of oceanic carbon monoxide to the atmosphere

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Abstract. Carbon monoxide (CO) is produced photochemically in the surface ocean and emitted to the atmosphere. To assess the magnitude of this ocean-atmosphere flux, seawater and atmospheric CO mole fractions were measured on six cruises throughout the Pacific Ocean from 1987 to 1994. The results showed consistent regional and seasonal variations in surface seawater CO concentrations with daily averaged concentrations ranging from 0.1 to 4.7 nM. Based on the concentration fields, the data were divided into four seasons and 10 latitude zones from 75°S to 75°N. Using monthly Comprehensive Ocean-Atmosphere Data Set wind and surface seawater temperature data and the Wanninkhof [1992] wind speed/transfer velocity relationship, the calculated zonal average fluxes ranged from 0.25 to 13 $\mu\text{mol}/\text{m}^2/\text{d}$. The combined seasonal and zonal fluxes result in a total global flux of 0.46 Tmol CO/y with 2/3 of this flux in the southern hemisphere. The estimated uncertainty in this number is approximately a factor of 2.

Introduction

Carbon monoxide (CO) is the major sink of the hydroxyl radical in the troposphere and hence strongly affects the oxidizing capacity of the atmosphere and the concentrations of other trace gases [Intergovernment Panel on Climate Change (IPCC), 1990; Thompson, 1992]. In order to be able to predict future atmospheric concentrations of radiatively important trace gas and aerosol species, climate chemistry models must include accurate estimates of the sources of CO to the atmosphere. At this time there are still large uncertainties in all the major sources of this gas [IPCC, 1990]. The observed increases in northern hemisphere atmospheric CO concentrations during the past decades [Khalil and Rasmussen, 1984; Novelli et al., 1992], the unexpected recent decrease in this trend [Khalil and Rasmussen, 1994; Novelli et al., 1994], and current discrepancies in CO budget/distribution analyses [Bakwin et al., 1994] emphasize the need for improved estimates of atmospheric CO sources and sinks.

The ocean was identified as a source of CO to the atmosphere in the early 1970s [Swinerton et al., 1970; Junge et al., 1971; Lamontagne et al., 1971; Linnenbom et al., 1973; Seiler, 1974]. Subsequent measurements [Conrad et al., 1982; Bates et al., 1993] have confirmed that the ocean is ubiquitously supersaturated with respect to atmospheric CO mole fractions resulting in a net flux to the atmosphere. The estimated magnitude of this

source ranges from 0.36 to 7.9 Tmol/yr [Junge et al., 1971; Linnenbom et al., 1973; Seiler and Schmidt, 1974; Conrad et al., 1982; Erickson, 1989]. Although the oceanic source is only 0.4 to 9% of the total sources to the atmosphere [IPCC, 1990], recent model sensitivity calculations suggest that the ocean may account for 5 to 50% of the boundary layer CO burden over large oceanic regions [Erickson and Taylor, 1992]. Consequently, oceanic CO may play a role in marine boundary layer photochemistry.

As a result of the high seawater supersaturations, the sea-to-air flux of CO is largely controlled by the seawater CO concentration. The concentration of CO in surface seawater is a function of photochemical production [Wilson et al., 1970; Lamontagne et al., 1971; Conrad et al., 1982], microbial consumption [Conrad et al., 1982; Conrad and Seiler, 1980, 1982; Jones, 1991], air-sea exchange [Conrad et al., 1982; Butler et al., 1987], and physical mixing processes (J. E. Johnson and T. S. Bates, Sources and sinks of carbon monoxide in the mixed layer of the tropical South Pacific Ocean, submitted to *Global Biogeochemical Cycles*, 1995) (hereinafter referred to as Johnson and Bates, submitted manuscript, 1995). The resulting lifetime of CO in surface seawater ranges from hours to a few days [Conrad et al., 1982; Jones, 1991; Johnson and Bates, submitted manuscript, 1995]. As a result of these various processes, the concentration of CO in surface seawater varies diurnally, regionally, and seasonally. Current oceanic flux estimates, however, are based on a database of limited temporal and spatial coverage with a majority of the measurements made in low latitudes and summer months. The limitations could potentially lead to a large bias in current CO flux estimates.

In an effort to reassess the ocean-atmosphere flux of CO, we have made measurements of CO mole fractions in surface seawater and the overlying atmosphere on six latitudinal transects 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 four seasons and recalculated the oceanic source of CO to the atmosphere. The complete CO data set is available via the internet at <http://saga.pmel.noaa.gov>.

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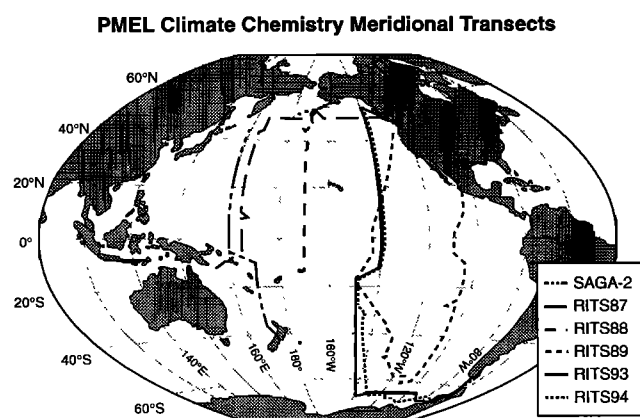


Figure 1. PMEL atmospheric climate chemistry meridional cruise tracks.

Methods

Sampling

Surface seawater entered the ship via a forward intake line located approximately 5 m below the water line (5 ± 5 m depending on sea state). The water was pumped at a high flow rate (approximately 100 L/min) 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. E. Johnson *et al.*, manuscript in preparation, 1995], consisted of a 20-L enclosed headspace continuously showered with 15–20 L/min of seawater. Every 48 min (1987–1990) or 60 min (1992–1994), approximately 50 mL of gas were withdrawn from the headspace to flush the sample loop and 2 mL (1987–1990) or 3 mL (1992–1994) were injected into the analytical system for analysis. Field comparisons of daily mean seawater CO concentrations from the Radiatively Important Trace Species (RITS) 1994 cruise showed that the equilibrator sampling technique for CO produced similar results as a standard purge and trap technique (J. E. Johnson *et al.*, manuscript in preparation, 1995). Field studies using different sampling techniques (pumping system, buckets, niskin bottles) showed no consistent differences in the CO concentrations in the upper 5 m of the ocean surface. Field tests with the equilibrator shrouded in dark plastic showed that CO was not photochemically produced in the equilibrator.

Air samples were pulled 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 8–10 L/min. Dekoron tubing was also used to connect the equilibrator to the analytical system. Laboratory tests showed that there was no production or loss of CO in the Dekoron tubing.

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

Cruise	Date	Location
(1) SAGA 1987 (<i>Akademik 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
May 7, 1993	Seattle, Washington	
(8) RITS 1994 (<i>Surveyor</i>)	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	

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. An analysis of the temperature data from 1987 to 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°C warmer than the intake water temperature due to heating from the pump and transit through the piping to the equilibrator.

CO Measurements

CO mole fractions 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). The mercury bed in the MBD was changed annually before each cruise to optimize the response of the detector. Samples from the air sampling line, the equilibrator, or a standard gas stream were dried using phosphorous pentoxide (1987–1990) or magnesium perchlorate (1992–1994) and drawn into the sample loop connected to an automated sample valve. CO, CO₂, and CH₄ 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 (1987–1990) or an E-Labs chromatography system (1992–1994). The sampling-gas chromatography-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.

CO standards in the range of 40 to 300 ppb (mole fraction) were dried, whole air mixtures contained in aluminum cylinders. Three cylinders were initially filled and calibrated for CO by the National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory (CMDL) in 1987. Standards in the range of 1000 to 3085 ppb were synthetic mixtures prepared by specialty gas companies. Two of the original three cylinders, along with five additional cylinders, were recalibrated by NOAA/CMDL in 1991. CO mole fractions in the seven primary standards, ranging from 71 to 3085 ppb, were referenced to the CMDL calibration scale [Novelli *et al.*, 1991]. The standards used during the cruises were chosen to bracket the ambient air and seawater mole fractions. Since the 3085 ppb CO standard is higher than the CMDL standard scale, this standard (used for seawater CO measurements in equatorial regions) had the highest uncertainty in its accuracy (approximately ±10%). The uncertainties of the other standards were ≤2% below 250 ppb and ≤5% above 250 ppb (P. Novelli, personal communication, 1995). The response of the Pacific Marine Environmental Laboratory (PMEL) CO detector was linear ($r^2 = 0.99$) within the usual working range (40 to 3085 ppb). Some equatorial seawater samples were outside this range and therefore may be underestimated by as much as 20% (J. E. Johnson *et al.*, manuscript in preparation, 1995). During each cruise the instrument precision, as determined by the average percent standard deviation of the standard response over a 6-hour period, ranged from 1 to 2%.

Data Reduction

The data were visually filtered to eliminate any episodes of ship contamination. These episodes were clearly apparent when the ship was running downwind by the extremely high CO

values (greater than 10 times ambient). CO dry-air mole fractions in both air ($(X)_a$) and equilibrator ($(X)_e$) samples were then computed using peak area and a 6-hour running-mean single-point standard and binned into hourly intervals. Gas solubilities in mmol/L/atm were calculated for each hourly CO value at both the local surface seawater temperature and equilibrator temperature using the local seawater salinity and the equilibrium solubility equations of *Wiesenburg and Guinasso* [1979]. CO mole fractions measured in the equilibrator ($(X)_e$) were corrected to a surface seawater CO mole fraction ($(X)_w$) using the ratio of the gas solubilities at the two temperatures. This correction reduced $(X)_e$ by approximately 0.58%. The concentrations and fluxes calculated here make no attempt to correct for any temperature [Katsaros, 1980] or concentration difference between the water inlet depth and the surface microlayer. Although we observed no indication of a concentration gradient in the upper 5 m of the water column, we cannot rule out the existence of such a gradient on calm days.

The temperature-corrected CO mole fractions were used to calculate $\Delta p\text{CO}$ in units of microatmospheres,

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

where $\Delta p\text{CO}$ is the difference in the air and seawater partial pressures of CO, P_a is the atmospheric pressure, and P_w is the saturation water vapor calculated at the local sea surface temperature and salinity according to *Weiss and Price* [1980]. The nanomolar concentration of CO in surface seawater was calculated as the product of the gas solubility and the seawater CO partial pressure. The $\Delta p\text{CO}$ and nanomolar data were then binned into daily averages.

Results and Discussion

Atmospheric CO Mole Fractions

Atmospheric CO mole fractions ranged from 40 to 260 ppb with a sharp interhemispheric CO gradient at the intertropical convergence zone, especially in the central and eastern Pacific Ocean (Figure 2). Background CO mole fractions ranged from 40 to 60 ppb and 110 to 130 ppb in the southern and northern hemispheres, respectively. Regions of higher values (e.g., 42°N on RITS 1993) were clearly associated with continental air masses based on air mass back trajectories and aerosol chemical and physical data (D. S. Covert *et al.*, Physical properties of marine boundary layer aerosol particles of the mid-Pacific in relation to sources and meteorological transport, submitted to *Journal of Geophysical Research*, 1995). The highest values, measured off the Kamchatka Peninsula during the 1987 Soviet American Gas and Aerosol Experiment (SAGA 1987), were a result of the great Chinese fire of 1987 [Cahoon *et al.*, 1991]. The lowest values from these cruises were measured in the austral summer in the southern hemisphere (RITS 1993), which is consistent with the general seasonal cycle and north-south gradient of atmospheric CO mole fractions [Novelli *et al.*, 1992]. Since the cruise tracks were purposely chosen to assess the regional and seasonal variations in seawater CO partial pressures, there is very little overlap in time and space among the six cruises. Thus it is difficult to assess interannual trends in the atmospheric levels of CO from these data.

The data reported here are consistent with the baseline station data of the NOAA Climate Monitoring and Diagnostics Laboratory. Direct comparisons with the CMDL data set are difficult due to both longitudinal and temporal (hourly samples aboard

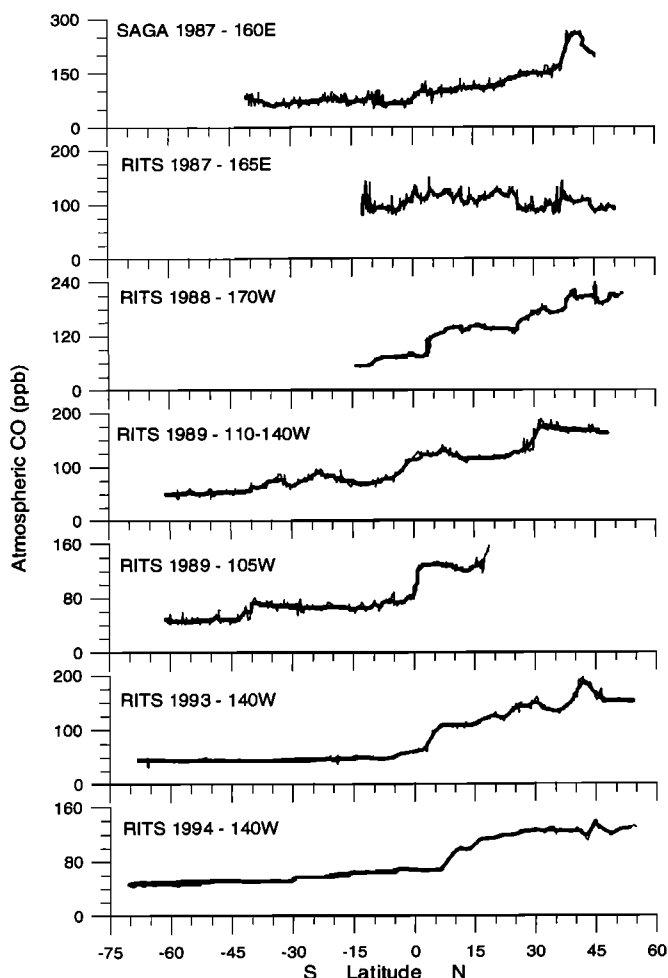


Figure 2. Atmospheric CO mole fractions in parts per billion along the meridional cruise tracks. The dark lines are a 12-hour running mean of the data.

ship versus weekly flask samples) differences in sampling. Nevertheless, in regions where the CO mixing ratio has small latitudinal gradients and little seasonal variation [Novelli *et al.*, 1992], the shipboard measurements agree well with the baseline station data. For example, the monthly mean CO mole fractions at American Samoa (14.2°S , 170.5°W) were 51.6 ± 2.7 ppb ($n = 4$) in April 1993 and 54.9 ± 3.8 ppb ($n = 4$) in December 1993 (P. Novelli, personal communication, 1995). The average CO mole fractions between 15°S and 14°S at 145°W measured during RITS 1993 (April 1993) and RITS 1994 (December 1993) were 48.2 ± 2.5 and 63.2 ± 0.4 ppb, respectively.

Seawater CO Concentrations and Saturation Ratios

Surface seawater CO concentrations throughout the Pacific Ocean ranged from 0.10 to 5.8 nM and exhibited a strong diurnal variation. A detailed description of the diurnal variations and the processes controlling the concentration of CO in surface seawater will be presented elsewhere (Johnson and Bates, submitted manuscript, 1995). Daily averaged concentrations ranged from 0.12 to 4.7 nM (Figure 3). Although the major focus of this work was on open ocean measurements, there was no evidence of elevated CO concentrations in the coastal regions sampled.

Most of the previous measurements of surface seawater CO concentrations were made in the 1960s and 1970s. The average concentrations for the various areas investigated were Arctic, 2.5 nM; North Atlantic, 3.1 nM; North Pacific, 2.7 nM; South Pacific from the equator to Antarctica, 3.6 nM [Swinerton and Lamontagne, 1974]; and Atlantic, 2.2 nM [Seiler, 1974]. These averages are within the range of measured values but approximately 2 times higher than the average values reported here. The differences could be the result of several factors including seasonal variations (most of the previous data were collected in the summer), regional variations (the previous Pacific Ocean data were from the central and eastern regions), frequency of sampling (different numbers of measurements over a 24-hour period), accuracy of the standards and/or a change in oceanic CO concentrations during the past 20 years. Unfortunately, it is not possible to resolve the relative importance of these factors with the available data.

Saturation ratios (SR), which are the ratio of the measured mole fractions in air equilibrated with seawater to the measured mole fractions in the overlying atmosphere [$(X)_w/(X)_a$], are useful in indicating deviations from equilibrium. Daily averaged Pacific Ocean SR ranged from 1.4 to 83 (Figure 4), with patterns similar to seawater CO concentrations (Figure 3). The regionally and seasonally averaged SR was 17. Saturation ratios in the Atlantic Ocean, measured by Conrad *et al.* [1982] ranged from 1 to 50 with a latitudinally normalized average value of 10.

Since the main purpose of this study was to calculate an ocean-atmosphere CO flux, the seawater CO data were com-

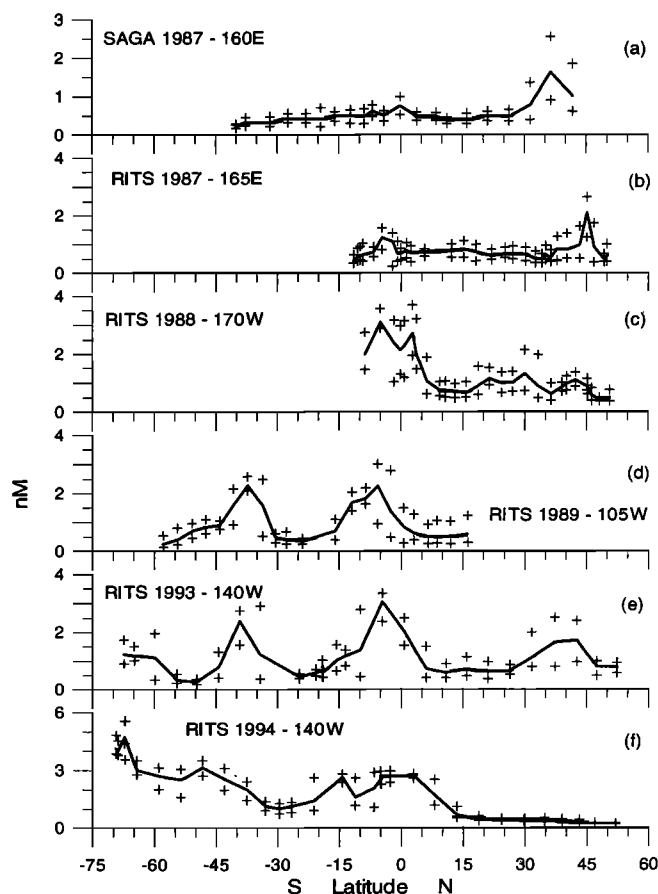


Figure 3. Averaged daily surface seawater CO concentrations in nanomoles per liter along the meridional cruise tracks. The pluses show the maximum and minimum concentrations each day.

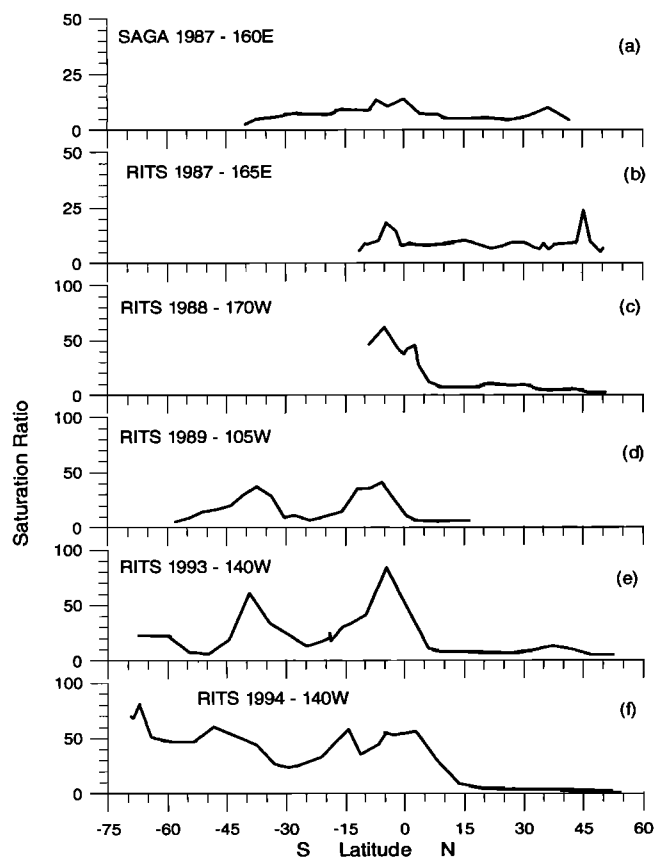


Figure 4. Saturation ratios along the meridional cruise tracks.

pared with some of the common oceanographic and meteorological parameters measured aboard the ship in an effort to identify a means by which to extrapolate the CO data both seasonally and regionally. Although no single parameter (solar radiation, wind speed, chlorophyll fluorescence, seawater nitrate, or temperature) correlated with surface seawater CO concentrations, the CO distribution with latitude showed consistent patterns from year to year (Figure 3). High surface seawater CO concentrations were found in the eastern and central equatorial Pacific Ocean (Figures 3c–3f) associated with the South Equatorial Current and equatorial upwelling (evident from the elevated nitrate concentrations). Concentrations in the western equatorial Pacific Ocean (Figures 3a and 3b) were significantly lower, consistent with the reduced upwelling and biological productivity in that region [Wyrki, 1981]. Surface seawater CO concentrations were generally low in the central gyres of the North and South Pacific Ocean (15° to 30°) and elevated again in the region of the subtropical convergences (30° to 45°). In the higher latitudes, surface seawater CO concentrations were highest near the summer solstice, lowest around the winter solstice, and intermediate at the equinox, which are consistent with a photochemical production source. On a regional basis, the southern hemisphere data reported here are qualitatively identical to the data of Swinnerton and Lamontagne [1974] collected in 1972. Their average concentrations, however, are approximately a factor of 2 higher than those reported here.

Based on the regional and seasonal features in the surface seawater CO concentrations measured between 1987 and 1994 (Figure 3), the data were averaged into ten 15° zonal regions and four seasons (Table 2). These 15° zones 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 CO concentrations than other oceanographic features such as chlorophyll. The data from March/April/May were used for both equinox seasons (March–May and September–November). No seasonal variations were observed in the tropical data (15° S to 15° N) so only annual averages are reported. The average values for the six cruises in the tropical waters takes into account the lower concentrations in the western equatorial Pacific Ocean. Blank values in Table 2 indicate regions without data. Based on the average 95% confidence interval for the daily averaged mean concentrations in each latitude zone, the estimated uncertainty in the zonal average surface seawater concentrations is $\pm 30\%$.

CO Air-Sea Exchange

The ocean-atmosphere flux (F) of CO can be expressed as

$$F = K_l L \Delta p_{CO} \quad (2)$$

where K_l 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 Δp_{CO} is the CO partial pressure difference between surface seawater and the overlying atmosphere. K_l can be parameterized using wind speed and Schmidt number, which is the ratio of kinematic viscosity of seawater and 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, which results in approximately a factor of 2 difference in the calculated gas fluxes [Wanninkhof, 1992]. The choice of wind speed/transfer velocity relationships and wind fields depend 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 certainly an important consideration if the local wind speed significantly affects the surface seawater CO concentration. However, contrary to the data of Conrad *et al.* [1982], we observed no significant anti-correlation between the wind speed measured aboard ship and the surface seawater CO partial pressures. Since the main purpose of this study was to estimate regional and seasonal ocean-atmosphere CO fluxes rather than instantaneous fluxes, we have chosen to use seasonal ocean wind speeds and seasurface temperatures (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].

Daily averaged CO partial pressures were used to calculate daily Δp_{CO} values from the six cruises (equation (1)). The Δp_{CO} values and the monthly $2^{\circ} \times 2^{\circ}$ COADS SST and wind speed (u in meters per second) data were averaged zonally and seasonally (Table 2). COADS SSTs were used to calculate gas solubilities [Wiesenburg and Guinasso, 1979] and diffusivities [Wise and Houghton, 1968]. 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) (580 at 20° C and a salinity of 35 ppt) for each region and season. Finally, the regional and seasonal CO transfer velocities in centimeters per hour were calculated according to Wanninkhof [1992] where

Table 2. Regional and Seasonal Seawater CO Concentrations, Seawater/Atmospheric CO Partial Pressure Differences, Seawater Temperature, Wind Speeds, CO Solubilities, and Transfer Velocities

Region	Cruise Number	Seawater CO Concentration, nM	$\Delta p\text{CO}_2$, μatm	SST, $^{\circ}\text{C}$	Solubility, mmol/L/atm	Wind Speed, m/s	Transfer Velocity (k_t), m/d
<i>March/April/May</i>							
60°–75°S	4,7	0.99	0.74	0.13	1.27	8.10	3.28
45°–60°S	4,7	0.55	0.46	6.11	1.11	9.10	5.10
30°–45°S	4,7	1.39	1.51	17.32	0.90	7.34	4.73
15°–30°S	4,7	0.64	0.82	24.82	0.79	6.26	4.26
0°–15°S	1–8	1.47	1.86	27.92	0.76	5.14	3.13
0°–15°N	1–8	0.99	1.18	27.85	0.76	5.62	3.73
15°–30°N	1,3,7	0.72	0.76	23.84	0.81	6.44	4.39
30°–45°N	1,3,7	1.13	0.99	14.47	0.94	7.80	4.90
45°–60°N	3,7	0.64	0.37	5.52	1.13	8.60	4.46
60°–75°N	—	—	0.37	2.47	1.20	7.11	2.74
<i>June/July/August</i>							
60°–75°S	—	—	0.10	0.57	1.26	6.27	1.99
45°–60°S	—	—	0.10	4.98	1.14	8.87	4.66
30°–45°S	1	0.26	0.21	14.36	0.94	8.15	5.33
15°–30°S	1	0.36	0.38	22.13	0.83	6.70	4.53
0°–15°S	1–8	1.47	1.86	26.25	0.78	6.31	4.51
0°–15°N	1–8	0.99	1.18	27.86	0.76	5.94	4.17
15°–30°N	2	0.68	0.77	26.50	0.78	6.20	4.38
30°–45°N	2	0.66	0.66	20.59	0.85	5.98	3.46
45°–60°N	2	1.77	1.64	10.62	1.01	6.63	3.14
60°–75°N	—	—	1.64	5.35	1.13	5.72	1.96
<i>September/October/November</i>							
60°–75°S	—	—	0.74	–0.45	1.29	7.53	2.77
45°–60°S	—	—	0.46	4.63	1.15	8.92	4.66
30°–45°S	—	—	1.51	14.30	0.95	7.48	4.48
15°–30°S	—	—	0.82	22.10	0.83	6.39	4.12
0°–15°S	—	—	1.86	26.16	0.78	5.75	3.73
0°–15°N	—	—	1.18	27.87	0.76	5.34	3.37
15°–30°N	—	—	0.76	26.57	0.77	6.27	4.49
30°–45°N	—	—	0.99	20.14	0.85	7.62	5.54
45°–60°N	—	—	0.37	9.81	1.03	9.31	6.03
60°–75°N	—	—	0.37	3.99	1.16	7.95	3.62
<i>December/January/February</i>							
60°–75°S	8	3.81	2.87	–0.10	1.28	6.09	1.84
45°–60°S	8	2.63	2.29	6.15	1.11	8.85	4.83
30°–45°S	8	1.88	1.98	17.61	0.89	6.78	4.07
15°–30°S	4,8	0.91	1.09	24.88	0.79	6.03	3.96
0°–15°S	1–8	1.47	1.86	27.29	0.77	5.17	3.11
0°–15°N	1–8	0.98	1.18	27.20	0.77	6.23	4.51
15°–30°N	8	0.41	0.39	23.61	0.81	7.03	5.20
30°–45°N	8	0.30	0.21	14.63	0.94	9.40	7.15
45°–60°N	8	0.19	0.06	5.60	1.12	10.68	6.90
60°–75°N	—	—	0.06	3.35	1.18	8.67	4.21

See Table 1 for cruise number. SST and wind speed from the COADS (Comprehensive Ocean-Atmosphere Data Set). Solubilities from *Wiesenburg and Guinasso* [1979]. Transfer velocities calculated from *Wanninkhof* [1992].

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

For comparison, CO transfer velocities were calculated for the hourly RITS 1994 data using both shipboard winds and the transfer velocity/wind speed relationship of *Liss and Merlivat* [1986]. The shipboard winds during the RITS 1994 cruise were

on average 30% higher than the 40-year climatological COADS winds (Table 3). The average transfer velocity calculated using shipboard winds and the *Wanninkhof* [1992] short-term wind speed/transfer velocity relationship was 46% higher than the average transfer velocity calculated using COADS winds and the *Wanninkhof* [1992] long-term wind speed/transfer velocity

Table 3. Average Wind Speed and Transfer Velocities From the Hourly RITS 1994 Cruise Data

Wind Field	Wind Speed, m/s	Wanninkhof [1992], m/d	Liss and Merlivat [1986], m/d
COADS	7.4 ± 1.5^a	4.7 ± 2.0^b	2.3 ± 0.94
Shipboard	9.6 ± 3.3	6.9 ± 4.7^c	3.8 ± 2.5

^aSeasonally and zonally averaged data.

^bCalculated using the Wanninkhof [1992] long-term wind speed proportionality factor (0.39).

^cCalculated using the Wanninkhof [1992] short-term wind speed proportionality factor (0.31).

relationship. Finally, the average transfer velocity calculated using shipboard winds and the Liss and Merlivat [1986] wind speed/transfer velocity relationship was 20% lower than the average transfer velocity calculated using COADS winds and the Wanninkhof [1992] long-term wind speed/transfer velocity relationship (Table 3).

Transfer velocities from (3), solubilities, and $\Delta p\text{CO}$ values (Table 2) were used to calculate the regional and seasonal fluxes using (2). Fluxes ranged from a winter low in the high latitudes of $0.25 \mu\text{mol}/\text{m}^2/\text{d}$ to a summer high of $13 \mu\text{mol}/\text{m}^2/\text{d}$. The average equatorial flux was $4.3 \mu\text{mol}/\text{m}^2/\text{d}$ and the average global flux was $3.4 \mu\text{mol}/\text{m}^2/\text{d}$. Regional annual CO emissions (the product of the flux and regional area) ranged from 6.6 to 97 Gmol/yr with 2/3 of the emissions in the southern hemisphere. The total annual ocean CO emission was 460 Gmol (Table 4). This value is clearly at the lower end of the previously estimated range (360 to 7900 Gmol/yr; see introduction); however, this estimate is the first to take into account seasonally and regionally averaged CO seawater partial pressures.

For comparison we have calculated oceanic CO emissions using both shipboard winds and the Liss and Merlivat [1986]

wind speed-transfer velocity relationship (Table 4). Calculations using ship winds are based on daily averaged fluxes rather than daily averaged $\Delta p\text{CO}$ values. The results of this comparison show that the wind speed-transfer velocity relationship used to calculate regional emissions from oceanic and atmospheric mole fraction measurements results in an uncertainty of approximately $\pm 50\%$. The other major uncertainties include the regionally and seasonally averaged CO seawater partial pressures ($\pm 30\%$, see above section on seawater CO concentrations) and the wind fields used for calculating transfer velocities ($\pm 30\%$ [Murphy et al., 1991; Wanninkhof, 1992], Table 3). When these uncertainties are summed in quadrature, the overall estimated uncertainty in the oceanic CO flux is approximately a factor of 2.

Conclusions

The ocean is ubiquitously supersaturated with CO with respect to the atmosphere resulting in a net flux to the atmosphere ranging seasonally and regionally from 0.25 to $13 \mu\text{mol}/\text{m}^2/\text{d}$. However, the total annual emission to the atmosphere of 0.46 Tmol or 13 Tg is small compared to current

Table 4. Regional Emissions of CO From the Ocean to the Atmosphere in Gigamoles per Year

Region	Area, ^a 10^6 km^2	Wanninkhof ^b		Liss and Merlivat ^c	
		COADS	Ship	COADS	Ship
60°–75°S	19.3	22	41	11	23
45°–60°S	39.0	63	83	31	44
30°–45°S	46.8	90	127	46	70
15°–30°S	46.1	44	46	22	26
0°–15°S	49.8	95	134	46	81
0°–15°N	49.5	64	76	32	43
15°–30°N	39.0	34	52	17	30
30°–45°N	27.9	32	32	16	18
45°–60°N	16.6	15	26	7	14
60°–75°N	8.5	5	13	3	7
Southern hemisphere	200	310	430	160	240
Northern hemisphere	140	150	200	76	110
Total	340	460	630	230	360

All emissions are seasonally averaged. Emissions based on the COADS winds are calculated from the average $\Delta p\text{CO}$ (μatm) for each season in each zone. Emissions calculated with the ship winds are calculated from the average daily flux ($\mu\text{mol}/\text{m}^2/\text{d}$) for each season in each zone.

^aRegional area from Levitus [1982].

^bFluxes calculated using transfer velocities from Wanninkhof [1992]. Fluxes based on the COADS winds were done with the long-term wind speed proportionality factor of 0.39. Fluxes based on ship winds were done with the short-term wind speed proportionality factor of 0.31.

^cFluxes calculated using the wind speed-transfer velocity relationships of Liss and Merlivat [1986].

Table 5. Sources of Carbon Monoxide to the Atmosphere (Tg(CO)/yr)

	Anthropogenic	Natural	Range
<i>Combustion</i>			
Technological (5)	400		300–600
Biomass burning (3,4,5)	700		300–900
<i>Hydrocarbon Oxidation</i>			
Methane (2,5)	350	350	400–1000
Nonmethane hydrocarbons (5)	200	300	300–1000
<i>Other Sources</i>			
Plants (1,5)		130	50–200
Oceans (6)		13	6–30
Totals	1600	800	

Numbers in parentheses refer to references by 1, Logan *et al.* [1981]; 2, Khalil and Rasmussen [1990]; 3, Andreae [1991]; 4, Lobert *et al.* [1991]; 5, Müller [1992]; 6, this study.

estimates from both terrestrial natural and anthropogenic sources of 2400 Tg(CO)/yr (Table 5). Even in the southern hemisphere, which accounts for 2/3 of the oceanic emissions, the ocean source is relatively small (<1%) since both methane oxidation and biomass burning are large sources of CO in this hemisphere.

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