Changes in equatorial CO₂ flux and new production estimated from CO₂ and nutrient levels in Pacific surface waters during the 1986/87 El Niño

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ABSTRACT

The seasonal variabilities of the CO_2 system and dissolved nutrients (nitrate, phosphate, and silicate) in surface seawater of the central tropical Pacific Ocean before and during the 1986/1987 El Niño/Southern Oscillation (ENSO) warm event were observed as part of a ship-of-opportunity program. Beginning in late 1986 and continuing through 1987, there was a gradual increase in sea surface temperature (SST) and slight decrease of surface seawater salinity around the central equatorial region. These changes were accompanied by decreasing levels of dissolved nutrients, ocean-surface pCO₂, dissolved inorganic carbon ($\sum CO_2$) and net CO_2 evasion. In September 1987, equatorial SST was warmest while CO_2 evasion, pCO₂, $\sum CO_2$, and the dissolved nutrients reached their lowest levels. In September 1987, owing to the weakened equatorial upwelling, the supply of $\sum CO_2$ from deeper waters was reduced by about 97–194 mM m⁻² d⁻¹, while the low replenishment of nitrate represented a loss of about 17–34 mM C m⁻² d⁻¹ in new production. The evasion of CO_2 from the central equatorial Pacific between 5°S and 5°N [10°S and 10°N] was estimated to be about 1.2 M CO_2 m⁻² yr⁻¹ [0.9 M CO_2 m⁻² yr⁻¹ prior to the 1987 El Niño, but only 0.2 M CO_2 m⁻² yr⁻¹ [0.2 M CO_2 m⁻² yr⁻¹] during the El Niño.

1. Introduction

El Niño/Southern Oscillation (ENSO) events are large-scale natural phenomena which have been occurring at interval of 2-7 years in the eastern tropical Pacific Ocean (Enfield, 1989; Philander, 1990). The events are known to be associated with significant changes in oceanic properties such as sea surface temperature (SST), upwelling rates and biological activities in the Pacific waters (Cane, 1983; Barber and Chavez, 1983). These changes may have important roles in altering the partial pressure of CO₂ (pCO₂) in surface seawater which, in turn, modulate the rates of exchange of CO₂ between the ocean and the atmosphere. Results from various background monitoring stations show a very low or negative rate of increase in atmospheric CO₂ in the early stage of an ENSO event followed by a high growth rate in the later stage (Wong et al., 1984b; Keeling and Revelle, 1985; Conway et al., 1988; Gaudry et al., 1991). Significant correlations between the variation of atmospheric CO₂ levels with largescale changes in Pacific SST (Newell et al., 1978; Hanson et al., 1981; Elliott et al., 1991), or with the Southern Oscillation Indices (Bacastow, 1976; Bacastow et al., 1980) also have been obtained. Thus observation of the oceanic CO₂ system during ENSO events may help to interpret the variation in the sources and sinks of the global carbon cycle (Keeling et al., 1989). However, in the last decade, observations of pCO₂ and biological activities during the course of an ENSO event have only been partially attempted for both the central and the western Pacific (Feely et al., 1987; Fushimi, 1987; Inoue et al., 1987; Inoue and Sugimura, 1988a; 1988b).

In 1983, the Centre for Ocean Climate Chemistry at the Institute of Ocean Sciences initiated a ship-of-opportunity program as part of

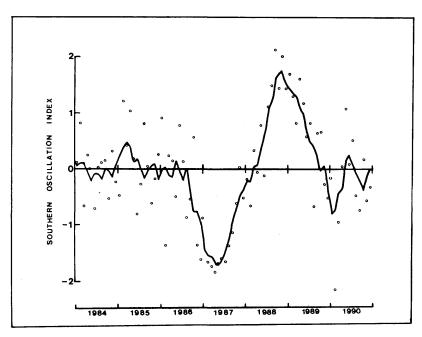


Fig. 1. Southern Oscillation Index, i.e., the difference between the standardized sea level pressure anomalies at Tahiti and Darwin (Tahiti-Darwin). Values are normalized by the mean annual standard deviation. The circles are individual monthly means and the curve shows the five-month running mean of the indices (adopted from World Meteorological Organization (1992)).

the Oceanic CO₂ Monitoring Project to study the carbon system of the Pacific Ocean (Wong et al., 1984a). Various properties of ocean surface waters along the ship routes were sampled periodically for several years. We report here our observations on the pCO₂ and nutrient concentrations in surface seawater near the central tropical Pacific before

and during the 1986/1987 El Niño (Fig. 1). This report presents the results of 13 north-bound cruises from March 1985 to February 1988 (Table 1). For consistence in interpretation of the results, observations taken on two earlier south-bound cruises or cruises that sailed off course for various reasons are excluded.

Table 1. The M/V Lillooet cruises

Cruise No.	Dates	Dates at 5°S-5°N
465N	12 Mar. 1985–29 Mar. 1985	19 Mar. 1985–21 Mar. 1985
469N	12 Aug. 1985-30 Aug. 1985	19 Aug. 1985-21 Aug. 1985
473N	16 Jan. 1986– 2 Feb. 1986	19 Jan. 1986-21 Jan. 1986
475N	23 Mar. 1986-13 Apr. 1986	1 Apr. 1986– 2 Apr. 1986
479N	1 Aug. 1986-19 Aug. 1986	9 Aug. 1986-11 Aug. 1986
481N	11 Oct. 1986–28 Oct. 1986	19 Oct. 1986
483N	14 Dec. 1986- 2 Jan. 1987	22 Dec. 1986-24 Dec. 1986
485N	21 Feb. 1987-12 Mar. 1987	1 Mar. 1987– 3 Mar. 1987
487N	1 May 1987-26 May 1987	11 May 1987-13 May 1987
489N	21 Jul. 1987-10 Aug. 1987	29 Jul. 1987- 1 Aug. 1987
491N	20 Sep. 1987- 8 Oct. 1987	28 Sep. 1987-30 Sep. 1987
493N	26 Nov. 1987-11 Dec. 1987	30 Nov. 1987- 3 Dec. 1987
495N	4 Feb. 1988-20 Feb. 1988	8 Feb. 1988-11 Feb. 1988

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2. Measurements

The ship-of-opportunity program was carried out on board the German container-carrier M/V Lillooet which sailed between Vancouver, Canada, and Australia 6 times a year. The north-bound route started from Brisbane, Australia, then visited Noumea, New Caledonia, and Sauva, Fiji. The route crossed the equator at about 170–180° W. Other ports-of-visit were Honolulu and Los Angeles or Oakland, USA. The last cruise was in February 1988.

2.1. CO₂ in atmosphere and surface seawater

The CO₂ sampling system installed on the ship was designed to measure both the contents of CO₂ in the atmosphere and in a dried aliquot of a gas phase equilibrated with surface seawater. The mole fractions of CO₂ were measured half-hourly by gas chromatograph with a flame-ionization detector (Weiss, 1981). A series of automated solenoid valves provided time-sequence sampling of marine air, equilibrated air, and a single CO₂-in-air standard obtained from the Scripps Institution of Oceanography.

The air intake installed on the deck structure of the M/V Lillooet was about 35 m above sea level with automated switching device to sample away from the smoke plume according to wind directions. Additional flask samples of marine air were also collected daily in quadruplicate. A shore-based nondispersive infrared analyzer was used to measure the mole fractions of atmospheric CO_2 in these samples.

A bellows-diaphragm pump delivered seawater at a rate of 20 l min⁻¹ from a sea chest in the engine room about 5 m below the waterline to a shower-type pCO₂ equilibrator (Keeling et al., 1965) situated at 15 m above sea level. The volumes of seawater and enclosed air in the equilibrator were 21 and 11 respectively. The seawater was being circulated continuously at a rate of about 3 l min⁻¹ in a loop of stainless steel tubings. This large pump rate and the thermal insulation on all pipes would keep the temperature difference between the intake and the equilibrator to within ±1°C under field condition for most of the time. For each sampling cycle, temperatures of seawater at the intake and in the equilibrator were recorded and their difference was used later to correct for the temperature effect on pCO₂ in seawater.

The position of the ship was relayed from a satellite navigation system directly to the microcomputer attached to the analyzing system. The printout from the computer included the analysis readings of CO₂ in the various sources, position of the ship, air temperature, salinity and seawater temperatures at the intake and in the equilibrator.

Additional meteorological records from the same Marsden Squares covering the cruise tracks were obtained from the National Climatic Data Center of NOAA, USA. The records included mean sea level pressure, wind speed, as well as wet-bulb and dry-bulb temperatures.

2.2. Dissolved nutrients and dissolved inorganic carbon

During all the cruises, samples of seawater at 5-m depth were collected at 1° latitude interval as regularly as possible for analysis later in a shorebased laboratory. Those samples for dissolved nutrients analyses were frozen immediately for storage at -10° C (Strickland and Parsons, 1972). Other samples were preserved by HgCl₂ to be analyzed later for dissolved inorganic carbon (also referred to as total carbon dioxide, $\sum CO_2$ (Wong, 1970). The levels of dissolved nitrate, phosphate, and silicate were measured by colorimetric methods (Strickland and Parsons, 1972) using a Technicon Autoanalyzer. The $\sum CO_2$ concentration was analyzed by gas chromatograph with a thermal conductivity detector (Weiss and Craig, 1973) with a measurement precision of about $\pm 0.3\%$.

3. Computations and data analyses

In early analyses of the data, the concentrations of atmospheric CO₂ from both the continuous and the flask samples were found to be highly variable. These samples might be contaminated and so none of these data were used in this report. Instead, we substituted the atmospheric CO₂ values in the dataset from Global Monitoring for Climatic Changes (GMCC), National Oceanic and Atmospheric Administration (NOAA), USA, as discussed below. For the equilibrium concentrations of seawater CO₂, the data also displayed fairly large variability. The extreme outliers were excluded for the subsequent analyses. When calculating the mean values of a given dataset, we employed a two-step averaging procedure. Those

data that lie beyond ± 2 standard deviations of the original mean value were again excluded. The selected data were then used again to calculate the final mean values.

3.1. Partial pressure of CO₂ in air

As mentioned in the above section, we derived the concentrations of atmospheric CO₂ during our cruises from the data observed at the network of GMCC stations operated by NOAA. For each sampling cycle, the atmospheric CO₂ level was estimated through two interpolation steps. The mole fractions of atmospheric CO₂ on the days when the ship crossed the same latitudes as those Pacific stations at American Samoa, Christmas Island, Cape Kumukahi, Sand Island, and Cape Meares were first interpolated from the respective CO₂ time series (Schnell and Rosson, 1986; 1987; Bodhaine and Rosson, 1988; Elkins and Rosson, 1989; Thoning et al., 1989; Waterman et al., 1989; World Meteorological Organization, 1989; 1990a; 1990b). Thus, for each cruise, we obtained a set of five values representing the spatio-temporal distribution of atmospheric CO₂ levels. The appropriate data were used to obtain by interpolation the mole fraction of atmospheric CO₂ for each GC sampling cycle at a given time and latitude. These interpolated values were converted to atmospheric pCO₂ (in μ atm) using the recorded barometric pressure and the saturated vapour pressure at SST. All the atmospheric pCO₂ values were assumed to be moisture-saturated at the air-sea interface.

3.2. Partial pressure of CO₂ in surface seawater

To compute the sea-surface pCO₂ (in μ atm), the mole fraction of CO₂ equilibrated with seawater was adjusted to a moisture-saturated basis using the vapor pressure of water and the in situ temperature. Any change in the value of pCO₂ due to temperature difference after sampling at the intake was corrected by the empirical temperature dependence given by Weiss et al. (1982). Since their function refers to CO₂ fugacity, we followed the equations given by Weiss (1974) to convert all CO₂ mole fractions to fugacities assuming saturated vapour at the air-sea interface. For easy comparison with other studies, the corrected CO₂ fugacities were converted back to values of CO₂ partial pressure (Wong and Chan, 1991).

3.3. Net CO, flux

The net flux of CO₂, F, across the air-sea interface (Keeling, 1968; Smethie et al., 1985; Wong and Chan, 1991) is computed as

$$F = k_{\mathbf{w}} s \, \Delta \mathbf{p} \mathbf{CO}_2, \tag{1}$$

where ΔpCO_2 is the excess of $pCO_2(sw)$, the CO_2 pressure exerted by the seawater, over $pCO_2(air)$, the partial pressure of CO_2 in the overlying air, k_w is the CO_2 transfer velocity and s is the solubility of CO_2 in seawater (Weiss, 1974) at specified salinity and temperature. The product $k_w s$, which is a convenient parameter to describe the state of the sea surface, is sometimes referred to as the CO_2 exchange coefficient K (Etcheto and Merlivat, 1988). The CO_2 transfer velocity was calculated from its relation with SST and wind speed at 10-m height for 3 different wind regimes (Liss and Merlivat, 1986; Liss, 1988), i.e.,

$$k_{\rm w} = 0.17 u_{10} ({\rm Sc}_{20}/{\rm Sc})^{2/3},$$

for $u_{10} \le 3.6,$ (2)

$$k_{\rm w} = [2.85u_{10} - 9.65](Sc_{20}/Sc)^{1/2},$$

for
$$3.6 < u_{10} \le 13$$
, (3)

$$k_{\rm w} = [5.9u_{10} - 49.3](Sc_{20}/Sc)^{1/2},$$

for
$$u_{10} > 13$$
, (4)

where k_w is the CO₂ gas transfer velocity (in cm h⁻¹), u_{10} is the wind speed (m s⁻¹) at 10-m height, Sc₂₀ and Sc are the Schmidt numbers at 20°C and at the SST respectively. We did not adjust for any chemical enhancement to the CO₂ gas transfer velocity. This enhancement was assumed to be negligible (Goldman and Dennett, 1983). However, Wanninkhof (1992) estimated that the theoretical effect of chemical enhancement at low wind speeds is about 6% enhancement at an average wind speed of 4.7 m s⁻¹ using the above Liss-Merlivat relationship.

Beginning from July 1987, we also had recorded wind speed at 1° latitude interval during the cruises. For these cruises, the observed wind data were used to compute the transfer velocities. For the other cruises, wind speeds were obtained from the database compiled by the National Climatic Data Center, USA. Since only a limited number of the data fall exactly on the Lillooet's cruise tracks, we arbitrarily decided to include wind speed data

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that were observed within a 50 km radius from the track and less than three hours before the time of the pCO₂ measurements. If more than one value was found, we used the one nearest to the exact location of the cruise track. Procedure for calculating the net CO_2 flux followed that described in Wong and Chan (1991).

4. Results

Table 2 gives the mean values of SST, salinity, dissolved nutrients and the dissolved inorganic carbon (normalized at 35.0 salinity) in surface seawater within the equatorial band $(5^{\circ}\text{S}-5^{\circ}\text{N})$ observed during the cruises. The averages of sea-surface pCO₂, Δ pCO₂, wind speed, the CO₂ exchange coefficient (K), and the net CO₂ flux within $10^{\circ}\text{S}-5^{\circ}\text{S}$, $5^{\circ}\text{S}-0^{\circ}$, $0^{\circ}-5^{\circ}\text{N}$, and $5^{\circ}\text{N}-10^{\circ}\text{N}$ are listed in Tables 3 to 7 respectively.

Fig. 2 shows the latitudinal and temporal variations in the salinity, SST, levels of dissolved nitrate and normalized $\sum CO_2$ in surface seawater between 15°S and 15°N for six of the cruises. Three of them show conditions during the boreal

Table 2. Averages of various oceanographic properties^{a)} in surface seawater near the central equatorial Pacific (5°S-5°N and 170°W-180°W) between March 1985 and February 1988

Cruise no.	SST (°C)	Salinity (psu)	PO ₄		SiO ₄ Σ μM kg	$\sum_{i=1}^{n} CO_2 _{S=35.0}$
465N	28.02	34.939	0.43	3.75	5.58	1999
469N	28.30	35.160	0.40	2.44	3.61	1990
473N	29.49	35.244	0.42	2.18	2.75	1966
475N	28.53	35.214	0.49	3.19	4.01	1982
479N	29.68	35.274	0.30	1.25	1.45	1955
481N ^{b)}	29.64	34.918	0.27	0.99	2.60	1933
483N	29.79	35.024	0.21	0.10	1.63	1960
485N	29.41	35.064	0.27	0.70	1.27	1962
487N ^{c)}	29.77	34.943	0.30	1.14	1.91	1934
489N	30.05	34.485	0.20	0.11	2.67	1945
491N	30.41	34.500	0.16	0.01	1.16	1993
493N	30.37	34.585	0.17	0.03	1.40	1934
495N	29.80	34.894	0.24	0.67	1.73	1946

^{a)} The values included are: sea surface temperature (SST), salinity, dissolved phosphate (PO₄), dissolved nitrate (NO₃), dissolved silicate (SiO₄), and normalized dissolved inorganic carbon ($\sum CO_2|_{S=35.0}$).

spring (April 1986, March 1987, February 1988) and the other three cruises represent conditions during the boreal autumn (August 1985, August, 1986, September 1987). Figure 3 depicts the variations in pCO₂(sw), ΔpCO₂, and CO₂ flux observed during the same cruises.

4.1. SST and salinity

Before the onset of the 1987 El Niño, e.g., August 1985 and April 1986, there was a trough of colder water between 5°S and 5°N where the minimal SST of about 27.5°C was at the equator (Fig. 2). The SST in this equatorial band averaged about 28.3°C in August 1985 to 29.5°C in January 1986 (Table 2). This band of colder water indicated the region of equatorial upwelling. As the ENSO conditions progressed, this trough became less prominent or even disappeared, and the mean SST between 8°S and 5°N increased gradually. Finally, an increase of about 2°C in mean SST was observed in September 1987. In March 1987 and September 1987, small troughs of slightly colder water were recorded but the locations of the minimum SST were displaced 1° northward (Fig. 2). Seasonally, the SST distributions during the boreal autumn were more or less symmetrical between north and south of the equator, whereas during the boreal spring, the SST south of 5°S were 2-5°C higher than those observed north of 5°N.

Surface salinity varied from cruise to cruise (Fig. 2). In August 1985 and April 1986, the salinity distribution peaked at 4°S. During the 1987 El Niño, the salinity distribution was bimodal with one peak at the equatorial region and another peak at 3-4°S or further south. The average salinity of the equatorial surface water decreased from 35.27 psu in August 1986 to 34.50 psu in September 1987 (Table 2).

4.2. Dissolved nutrients in surface seawater

In non-El Niño periods, the latitudinal distribution of dissolved nitrate, phosphate or silicate in surface seawater all showed the typical peak within the equatorial band due to upwelling of nutrient-rich deep waters. The level of all three nutrients dropped steeply outside of this region. For example, the level of dissolved nitrate decreased from $4-6~\mu{\rm M~kg^{-1}}$ at the equator to about $0.2~\mu{\rm M~kg^{-1}}$ between 10° and 15° latitudes (Fig. 2). For dissolved phosphate, the average level was about

b) No data from 0° to 6°S.

c) Crossing the equator at 160° W.

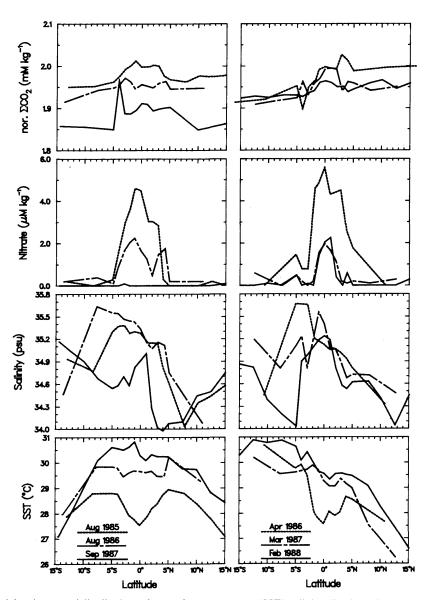


Fig. 2. Spatial and temporal distributions of sea surface temperature (SST), salinity, dissolved nitrate, and normalized dissolved inorganic carbon (nor. $\sum CO_2$) in surface seawater of the central tropical Pacific Ocean.

 $0.4 \,\mu\text{M kg}^{-1}$ within the equatorial band but decreased by about half outside of this region, and for dissolved silicate, from 4–5 μ M kg $^{-1}$ to 1.5–2 μ M kg $^{-1}$.

During the 1987 El Niño, nutrient levels in the equatorial surface water decreased to fairly low values. Especially in September 1987, the average level of all three nutrients remained near the mini-

mum values as the equatorial peaks disappeared altogether. The decrease was particularly obvious for nitrate as almost all the samples analyzed were below the sensitivity level of detection (Fig. 2).

4.3. $\sum CO_2$ in surface seawater

During non-El Niño periods, the average normalized $\sum CO_2$ in surface seawater was 1.97-2.00

mM kg $^{-1}$ near the equator, but was 1.90–1.95 mM kg $^{-1}$ within 10–15° north and south of the equator. From August 1986 to March 1987, the normalized \sum CO $_2$ decreased gradually, then dropped further to an average of 1.89 mM kg $^{-1}$ within the equatorial band in September 1987 (Table 2).

4.4. CO, partial pressure

The distributions of ocean-surface pCO₂ all showed the typical peak within 4°S-5°N (Fig. 3). During non-El Niño periods, another small peak appeared between 4°S and 7°S at the location of the second salinity peak mentioned earlier. For

these cruises, the equatorial pCO₂ reached about $400-415 \mu atm$ (Table 3) and ΔpCO_2 had a peak in supersaturation of $80-100 \mu atm$. Their values reduced by about half in October 1986 and March 1987 (Table 4; Fig. 3). In September 1987 and February 1988, the mean ΔpCO_2 within the equatorial band reduced further to only $11-14 \mu atm$ (Table 4).

During the boreal spring, ΔpCO_2 values decreased slowly north of 5° N, and surface ΔpCO_2 had negative values at about 15° N. However, ΔpCO_2 obtained during the boreal autumn decreased to minimum values at about 6° N and then increased gradually northward. South of 7° S,

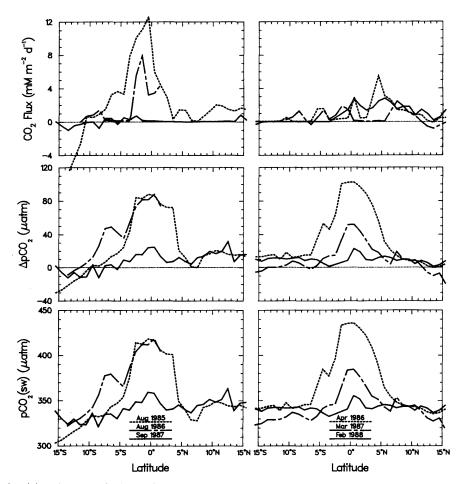


Fig. 3. Spatial and temporal distributions of various CO_2 properties near the central tropical Pacific Ocean. $pCO_2(sw)$: pCO_2 in surface seawater; ΔpCO_2 : difference in CO_2 partial pressures between the surface ocean and the overlying atmosphere $[pCO_2(sw) - pCO_2(air)]$.

Table 3. Averages of pCO₂ in surface seawater (in μ atm) observed near the central equatorial Pacific between 170° W and 180° W

Cruise Latitudinal zone					
no.	10°S-5°S	5°S–0°	0°-5° N	5° N-10° N	
465N	361.8	399.9	406.3	343.6	
469N	338.2	394.9	395.4	336.4	
473N	346.6	391.1	401.4	342.9	
475N	348.2	404.4	414.3	350.9	
479Na)	364.8	395.8	411.7		
481N ^{b)}	351.8		375.9	338.5	
483N	351.5	365.7	359.5	336.8	
485N	332.9	355.7	366.7	344.7	
487Nc)	351.4	381.1	376.8	351.0	
489N	339.5	342.7	339.1	354.4	
491N	332.1	347.3	346.2	344.0	
493N	342.9	353.6	356.9	339.5	
495N	341.5	337.4	346.7	343.8	

a) No pCO₂ data between 2°N and 10°N.

 ΔpCO_2 values reduced to about zero in non-El Niño years. In both 1986 and 1987, ΔpCO_2 values still maintained slight supersaturations of 5–15 μ atm during the boreal spring between 7°S and 15°S, while during the boreal autumn, ΔpCO_2 values were below the equilibrium level in water south of 13°S (Fig. 3).

Table 4. Averages of ΔpCO_2 (in μ atm) near the central equatorial Pacific between $170^\circ W$ and $180^\circ W$

Cruise	ruise Latitudinal zone					
no.	10°S-5°S	5° S–0°	0°-5° N	5° N-10° N		
465N	30.5	67.6	73.7	11.8		
469N	8.4	65.1	66.2	8.4		
473N	18.3	61.8	71.0	11.9		
475N	18.2	72.3	80.9	16.5		
479Na)	35.0	65.4	81.1	_		
481N ^{b)}	21.9		46.1	9.5		
483N	23.3	36.7	30.5	6.3		
485N	3.1	24.8	34.0	4.0		
487Nc)	20.3	48.6	42.3	15.9		
489N	6.7	10.3	6.1	22.2		
491N	-0.6	14.2	12.8	11.7		
493N	11.0	21.8	24.3	7.4		
495N	10.4	5.6	14.4	10.6		

a) No pCO₂ data between 2°N and 10°N.

4.5. Surface wind speed and CO₂ exchange coefficient

As expected, the estimated wind speeds were highly variable (Table 5). Prior to the 1987 El Niño, the average wind speeds observed within the 5°S-5°N band and that outside of this band were about 6 m s⁻¹ and 7 m s⁻¹, respectively. And within the equatorial band, the region north of the equator was slightly calmer than the southern zone. This relatively calm weather just north of the equator confirmed the observed position of the intertropical convergence zone. As the 1987 El Niño progressed, the average wind speeds also decreased gradually but then increased again, especially north of the equator, in late 1987 and February 1988 (Table 5). Wind speeds along the central tropical Pacific were also decreased in previous El Niño events (Harrison, 1987).

Etcheto and Merlivat (1988) pointed out that, since the effects of temperature on the $\rm CO_2$ transfer velocity $k_{\rm w}$ and on $\rm CO_2$ solubility nearly cancel one another, the $\rm CO_2$ exchange coefficient is primarily a function of wind speed. Thus variabilities of the $\rm CO_2$ exchange coefficients followed closely those of wind speeds (Table 6). Within the 5°S-5°N latitudinal zone, the estimated $\rm CO_2$ exchange coefficients for 1985 were generally higher than those for 1987 (Table 6). During the non-El Niño period from March 1985 to April 1986, the average was about 52 M m $^{-2}$

Table 5. Averages of the surface wind speed (in $m \, s^{-1}$) observed near the central equatorial Pacific between 170° W and 180° W

Cruise		Latitud	dinal zone	
no.	10°S-5°S	5°S–0°	0°-5° N	5° N-10° N
465N	4.6	5.4	3.8	9.2
469N	11.5	9.5	5.2	7.7
473N	2.5	6.3	5.7	10.4
475N	2.6	2.8	5.9	8.6
479N	4.2	5.6	5.6	_
481N	6.7	_	3.8	2.1
483N	7.3	5.7	3.4	4.3
485N	12.9	6.4	1.8	8.2
487Na)	3.0	2.5	3.4	5.1
489N	9.9	2.4	4.1	4.2
491N	7.0	5.0	3.0	1.6
493N	2.1	2.9	3.2	10.3
495N	0.5	5.7	10.5	11.9

a) Crossing the equator at 160° W.

b) No data between 0° and 6°S.

c) Crossing the equator at 160°W.

b) No data between 0° and 6°S.

c) Crossing the equator at 160° W.

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Table 6. Estimated CO_2 exchange coefficient (in $M m^{-2} d^{-1} atm^{-1}$) near the central equatorial Pacific between 170° W and 180° W

Cruise		Latituo	linal zone	
no.	10°S-5°S	5°S–0°	0°-5° N	5° N-10° N
465N	28	46	16	132
469N	182	137	43	98
473N	4	64	52	163
475N	7	6	57	117
479N	34	57	50	_
481N	75	_	17	3
483N	88	56	21	47
485N	241	75	2	113
487Na)	22	5	16	39
489N	147	7	22	23
491N	84	38	7	2
493N	3	10	10	164
495N	1	9	161	192

a) Crossing the equator at 160° W.

 d^{-1} atm⁻¹ within the 5°S-5°N zone, or about 79 M m⁻² d⁻¹ atm⁻¹ (2.9 × 10⁻² M m⁻² yr⁻¹ μatm⁻¹) within the 10°S-10°N band. The latter value was slightly higher than the range of 1.5–2.2 × 10⁻² M m⁻² yr⁻¹ μatm⁻¹ for the same region during the period July-October 1978 estimated by Etcheto and Merlivat (1988). Etcheto et al. (1991) also presented four maps at 2.5-degree resolution of the CO₂ exchange coefficients from August 1987 to May 1988. The average value from our cruise in February 1988 was about 4.5 × 10⁻² M m⁻² yr⁻¹ μatm⁻¹, which falls within the range of 2.9–5.8 × 10⁻² M m⁻² yr⁻¹ μatm⁻¹ given in their February 1988 map.

4.6. Net CO₂ flux

Evasions of CO_2 occurred mainly within the equatorial band. Before the onset of the 1987 El Niño, CO_2 fluxes in the boreal autumn were higher than those fluxes in the boreal spring. The effluxes observed in the August 1985 cruise showed a peak value of about 12 mM m⁻² d⁻¹ at the equator. This peak reduced to about 8 mM m⁻² d⁻¹ a year later in August 1986 (Fig. 3). The averages of CO_2 fluxes reduced gradually to less than 1 mM m⁻² d⁻¹ (Tables 7). In February 1988, the evasions of CO_2 started to increase again but occurred mainly in the oceanic area north of the equator.

Table 7. Estimated net CO_2 fluxes (in $mM m^{-2} d^{-1}$) near the central equatorial Pacific between $170^{\circ} W$ and $180^{\circ} W$

Cruise		Latitue	dinal zone	
no.	10°S-5°S	5°S–0°	0°-5° N	5° N-10° N
465N	1.3	3.7	0.9	0.9
469N	2.0	8.8	2.9	0.7
473N	0.1	3.9	3.4	2.0
475N	0.3	0.4	3.8	1.8
479Na)	0.6	4.5	4.0	
481N ^{b)}	1.5	_	0.8	*
483N	1.9	2.5	0.7	-0.2
485N	0.5	1.2	0.1	1.2
487Nc)	0.4	0.2	0.7	0.4
489N	0.8	0.1	0.2	0.5
491N	*	0.4	0.1	*d)
493N	*	0.2	0.1	1.1
495N	*	0.7	2.1	2.0

a) No pCO₂ data between 2°N and 10°S.

5. Discussion

In recent years, many workers have reported the changes in oceanographic conditions (McPhaden and Hayes, 1990; McPhaden et al., 1990) and chemical properties of surface seawater (Feely et al., 1987; Fushimi, 1987; Inoue and Sugimura, 1988a; 1988b) near the tropical Pacific during an ENSO event. The observed reduction in oceansurface pCO₂ validates qualitatively other modelling studies in which the physical, chemical and biological changes in the Pacific Ocean during an ENSO event are simulated (Volk, 1989; Siegenthaler, 1990). Our observations at the central tropical Pacific extend the results of Feely et al. (1987) for the 1982/1983 ENSO event. However, these results differ partly from the observations at western tropical Pacific (Fushimi, 1987; Inoue et al., 1987; Inoue and Sugimura, 1988a; 1988b).

5.1. Oceanographic properties during non-El Niño periods

¹⁴C distribution in the tropical Pacific water show that part of the excess atmospheric CO₂ absorbed in surface seawater of the subtropical gyres and at higher latitudes converge to the

b) No data between 0° and 6°S.

c) Crossing the equator at 160° W.

d) Less then 0.05 mM m⁻² d⁻¹.

equatorial region through isopycnal mixing and equatorward meridional advection (Quay et al., 1983; Broecker et al., 1985; Bryden and Brady, 1985). The converged water mass lies above the equatorial pycnocline at about 100-m depth and is the source of CO₂ in the tropical surface water. During non-El Niño periods, the latitudinal distribution of ΔpCO₂ (Fig. 3) always showed the typical equatorial peak which is attributed to the upwellings of these high-CO₂ subsurface waters. Keeling (1968), Takahashi et al. (1986) and Tans et al. (1990) have published contour maps of the spatial and seasonal variabilities of ΔpCO₂ values in the surface oceans. The ΔpCO_2 values observed during our 1985 and early 1986 cruises agree rather well with their results for the central Pacific region.

The oceanographic properties observed during our 1985 and early 1986 cruises were in the same ranges as those reported by Feely et al. (1987) in 1984 at 170° W. For example, SST values at the equator were about 27–27.5°C in all cases, and SST distribution of the southern limbs are higher than those of the northern limb. Furthermore, the magnitude of ΔpCO_2 in 1984 was the same as that in 1985, but 20% less than the average recorded in March 1986. From the same 1986 cruise, the levels of phosphate and nitrate in surface water were slightly higher than the measurements in 1984, but levels of surface silicate remained about the same in both years.

In the August 1986 cruise, oceanographic changes were detected. The disappearance of the cold water trough and the slight decrease in salinity near the equator (Fig. 2) implied the cessation or weakening of the equatorial upwelling. According to Lander (1989), this warm event in late 1986 was not a typical precursor to El Niño but was related to the anomalous westerlies prevalent in the central Pacific area observed at that time.

5.2. Changes associated with El Niño events

Our results showed that the changes in oceanic properties are reversed temporarily and partially in the early months of 1987. Nutrient and salinity peaks and a small trough of cold water reappeared at or near the equator. Probably in the onset phase of the 1987 El Niño, the equatorial easterlies were not totally diminished (Lander, 1989). According

to Charney and Spiegel (1971) and Feely et al. (1987), the occasional bursts of northeast trade winds across the equator would promote upwelling and could produce a slightly northward (upwind) displacement of the maximum upwelling zone.

Right at the equator during 1987, the ΔpCO_2 values were diminishing but never dropped below about 20 μ atm. In September 1987, nitrate was almost depleted (Table 1) and phosphate and silicate were reduced to fairly constant minimum levels. The almost complete utilization of nitrate under El Niño condition suggested it to be the limiting nutrient for the growth of phytoplankton in the mixed layer of this region.

During the 1987 El Niño, the changes in the oceanographic properties of surface waters in the central tropical Pacific were similar to those changes observed in 1983 at 158°W by Feely et al. (1987). Increasing SST and slight lowering of salinity could be detected in central and eastern equatorial Pacific waters during both warm ENSO events. Near saturation of seawater pCO₂ prevalent throughout the region east of the dateline were related to the failure of equatorial upwelling. Nutrients in surface waters were also found to be severely depleted, though the nutrient levels at 158°W might be slightly higher than those near the central Pacific (Feely et al., 1987).

During a warm ENSO event, changes in oceanographic properties at the central tropical Pacific differed from those reported for the equatorial area at 137°E (Fushimi, 1987; Inoue et al., 1987; Inoue and Sugimura, 1988a; 1988b) or the western Pacific in general (MacPhaden et al., 1990). For example, compared with non-El Niño years, the El Niño year of 1983 in the far western Pacific had lower temperatures and high salinities in surface water, as well as a 20 µatm increase in seawater pCO₂ near the equator in January. As pointed out by Fushimi (1987), upwelling might prevail over a wide area in the western North Pacific following the eastward displacement of warm water in the years with ENSO events. An enhanced upwelling in the far western Pacific could explain the observed changes in SST, salinity and pCO₂ in surface waters. Inoue and Sugimura (1988b) reported no change in the pCO₂ along 160°W in January 1987 and also during the non-El Niño periods. However, our extensive results indicated otherwise.

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5.3. Reduced supplies of surface $\sum CO_2$ and dissolved nitrate

During an El Niño, the decrease in the levels of dissolved nutrients and $\sum CO_2$ in surface seawater reflect the reduced replenishment of the upwelled waters with high nutrient and high CO₂. This change in nutrient levels in the surface seawater may be used to infer the decrease in photosynthetic uptake of CO₂ by phytoplankton. The almost exhaustion of mixed-layer nutrients in September 1987 allows us to estimate the maximum reduction of $\sum CO_2$ and nitrate supplies within the equatorial region during a moderate El Niño. We shall compute the reduction of $\sum CO_2$ and nitrate supplies within the 5°S-5°N equatorial band since the peaks of dissolved nutrients were mainly within this region (Fig. 2). The maximum effects from the El Niño were represented by the low values observed during the September 1987 cruise (491N). To normalize any seasonal effect and to exclude possible effects from the warm event in late 1986, the values from the August 1985 cruise (469N) were used to represent the non-El Niño levels.

The difference in the $\sum CO_2$ averages between cruises 469N and 491N (Table 2) is about 97 μ M kg⁻¹. If we take the upwelling velocity for this region of between 1 m d⁻¹ (Wyrtki, 1981) and 2 m d^{-1} (Halpern et al., 1989), the supply of $\sum CO_2$ in September 1987 is thus reduced by about 97–194 mM m⁻² d⁻¹. Similarly, the difference in the levels of nitrate is about 2.4-4.9 mM m⁻² d⁻¹. Using a Redfield ratio of 7 (Broecker and Peng, 1982), the decrease in nitrate by upwelling represents a reduced new production of 17-34 mM C m⁻² d⁻¹. From the map prepared by Berger et al. (1987), the primary production around the central equatorial Pacific ranges from 30 to 60 g C m⁻² yr⁻¹. Also, new production is estimated to be 17.8% of the primary production (Berger et al., 1987). Thus, the estimated range of new production at the central equatorial Pacific is about 15-30 mM C m⁻² d⁻¹. This range of values coincide remarkably well with our estimates based on the reduced supply of dissolved nitrate. The result from our observations reflect the maximum reduction of new production near the central equatorial Pacific during the height of the 1987 El Niño.

5.4. Reduced CO₂ evasion during El Niño

The variation in equatorial CO₂ fluxes (Table 7) during the ENSO periods reflect the spatial and

temporal variations in the ΔpCO_2 term (Table 4) and the CO₂ exchange coefficient (Table 6) along the equatorial Pacific. The highest fluxes come from the main equatorial upwelling region east of the dateline within 4°S-2°N. In non-El Niño periods, the area with high evasion rate in the eastern Pacific extends to about 10°S-10°N. The total flux and the areal extent decrease westwards to about 130°W (Feely et al., 1987; Fushimi, 1987). Under El Niño condition, CO₂ evasion in the eastern Pacific may be reduced drastically. However the evasion of CO₂ from the western Pacific could remain at the same level as that in non-El Niño periods or even increases substantially due to enhanced upwelling (Fushimi, 1987; Inoue et al., 1987). Thus our results from the central Pacific could only serve as an approximation of the average condition for the equatorial Pacific region. For our estimates, the average values from March 1985 to April 1986 are taken as representatives of non-El Niño condition, and averages from March 1987 to February 1988, El Niño condition. The May 1987 values are not used because the cruise was off course.

From our observations, the CO₂ fluxes from the equatorial band within 5°S-5°N averaged about $3.2 \,\mathrm{mM} \,\mathrm{CO}_2 \,\mathrm{m}^{-2} \,\mathrm{d}^{-1} \,(1.2 \,\mathrm{M} \,\mathrm{CO}_2 \,\mathrm{m}^{-2} \,\mathrm{yr}^{-1})$ during non-El Niño period and about 0.5 mM $CO_2 m^{-2} d^{-1}$ (0.2 M $CO_2 m^{-2} yr^{-1}$) during the 1987 El Niño. Thus, in response to this El Niño, the oceanic CO₂ flux to the atmosphere was reduced by about 1 M CO₂ m⁻² yr⁻¹ (Table 8). If the region of interest is extended to 10°S-10°N, then the effluxes of CO₂ to the atmosphere was about $0.9~{\rm M}~{\rm CO_2}~{\rm m}^{-2}~{\rm yr}^{-1}$ before the 1987 El Niño, but decreased to about $0.2~{\rm M}~{\rm CO_2}~{\rm m}^{-2}~{\rm yr}^{-1}$ in 1987 — a reduction of $0.7 \text{ M CO}_2 \text{ m}^{-2} \text{ yr}^{-1}$ (Table 8). Assuming these estimates represent the average condition of the tropical Pacific bounded by 10°S, 10°N, 80°W, and 135°E with an area of 35×10^6 km², then the efflux of CO₂ during the non-El Niño period and during the 1987 El Niño were about 0.4 Gt C yr⁻¹ and 0.1 Gt C yr⁻¹ respectively.

Our estimate of the net flux of CO₂ from the equatorial Pacific in 1985/1986 is less than the values of 0.6–1 Gt C yr⁻¹ for non-El Niño periods (Table 8) estimated by other workers (Keeling and Revelle, 1985; Smethie et al., 1985; Takahashi et al., 1986; Feely et al., 1987; Volk, 1989; Siegenthaler, 1990). Most of these flux values are

Table 8. Comparison of estimates of CO, evasion	ı fron	from i	the tropica	l Pacific
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Region of interest	Area (10^6 km^2)	Annual (M CO ₂ m ⁻²		Reference
Non-ENSO condition				
5°S, 5°N, 100°W, 170°E	11	4.5	0.6	Keeling and Revelle (1985
10°S, 10°N, 80°W, 150°E	31	2.2	0.8	Smethie et al. (1985)
10°S, 10°N, 80°W, 130°E	34.4	1.85	0.8	Takahashi et al. (1986)
10°S, 10°N, 80°W, 135°E	35	1.4	0.6	Feely et al. (1987)
10°S, 10°N, 80°W, 120°E	39	1.8	0.8	Volk (1989)
5°S, 5°N, 170°W, ·180°W		1.2		this report
10°S, 10°N, 170°W, 180°W		0.9	0.4*	this report
ENSO condition				
10°S, 10°N, 80°W, 135°E	35	0.05	0.02	Feely et al. (1987)
5°S, 5°N, 170°W, 180°W		0.19		this report
10°S, 10°N, 170°W, 180°W		0.21	0.09*	this report

^{*} Calculated using area of 35×10^6 km² for tropical Pacific Ocean.

calculated using different total area of the tropical Pacific region. Keeling and Revelle (1985) estimate a flux of 0.6 Gt C yr⁻¹ (4.5 M CO_2 m⁻² yr⁻¹) for the 10° equatorial band between 100°W and 170° E with an area of about 11×10^{6} km². This is the same region chosen by Wyrtki (1981) for his calculation of the rate of upwelling in the eastern tropical Pacific and is about one-third the area chosen by Takahashi et al. (1986), Feely et al. (1987) or Smethie et al. (1985). Keeling and Revelle (1985) also use a global average of the CO₂ transfer velocity which is three times larger than the equatorial average used by Feely et al. (1987), who also give an estimated evasion of 0.6 Gt C yr^{-1} (1.4 M CO₂ m⁻² yr⁻¹). The CO₂ evasion from the Pacific estimated by Smethie et al. (1985) is based on radon deficit measurements from the tropical Atlantic. Takahashi et al. (1986) estimate the CO₂ flux from the Pacific within $10^{\circ}\text{S}-10^{\circ}\text{N}$ to be $0.76\,\text{Gt}\,\text{C}$ or $1.85\,\text{M}\,\text{CO}_2$ $m^{-2}yr^{-1}$. The estimate of equatorial CO₂ evasion from the modelling study of Volk (1989) is about $1.8 \text{ M CO}_2 \text{ m}^{-2} \text{ yr}^{-1}$ or 0.8 Gt C yr^{-1} , which is also the same value obtained by Siegenthaler (1990) from model simulation. Recently, Murphy et al. (1991) have assessed the CO₂ flux in the South Pacific during austral autumn (February to May) using various wind-field datasets and the $K - u_{10}$ relationships by Liss and Merlivat (1986) and Tans et al. (1990). For the region 0°-15°S

and $160^{\circ}E-100^{\circ}W$, their estimates are about 0.4–1.8 M CO₂ m⁻² yr⁻¹.

The concentration of atmospheric CO₂ in the early stage of an El Niño shows a slow or negative rate of increase and then follows by a high growth rate in the later stage (Wong et al., 1984b; Conway et al., 1988). Elliott et al. (1991) also found from statistical analysis a tendency for the trend of the atmospheric CO₂ levels to dip before the main rise if the SST is rising quickly. The reduced evasion of CO₂ may be one of the factors causing the dip in CO₂ growth rate during the early stage of an El Niño. As CO₂ evasion to the atmosphere is still fairly low during the late stage of an El Niño, the observed increase in atmospheric CO₂ growth rate during this period strongly suggests the contribution from other major CO₂ sources. One of these sources is probably the tropical terrestrial biosphere (Elliott et al., 1991).

5.5. Uncertainties in CO₂ flux estimates

The study of Murphy et al. (1991) illustrates one of the uncertainties in estimating oceanic CO_2 flux. It concerns the choice of the $k_w - u_{10}$ or $K - u_{10}$ relationship. The Liss-Merlivat relationship (eqs. (2-4)) is derived using data from estimated radon deficit in lake and from wind tunnel experiments. Takahashi and his co-workers (Takahashi et al., 1986; Takahashi, 1989; Tans et al., 1990) also develop several $K - u_{10}$ relationships based on

wind-tunnel data as well as global ¹⁴C inventory data. The relationship used by Tans et al. (1990) is given as

$$K = 0, u_{10} \leqslant 3 (5)$$

$$K = 0.016(u_{10} - 3), u_{10} > 3,$$
 (6)

where u_{10} is wind speed (in m s⁻¹) at 10 m above the sea surface and K is the CO_2 exchange coefficient (in $M CO_2 m^{-2} yr^{-1} \mu atm^{-1}$). The constant 0.016 in eq. (6) represents a progressive refinement, though slightly lower value, from those derived previously by Takahashi et al. (1986) and Takahashi (1989). The global average CO₂ exchange coefficient estimated by the Liss-Merlivat relationship (Etcheto and Merlivat, 1988; Etcheto et al., 1991) is about half of that estimated by the relationship used by Takahashi et al. (1986). For the tropical Pacific region, Takahashi et al. (1986) use a CO2 exchange coefficient of $3.7 \times 10^{-2} \text{ M CO}_2 \text{ m}^{-2} \text{ yr}^{-1} \mu \text{atm}^{-1}$ for their CO₂ flux estimation. This value is about 27 % higher than the average from our 1985 cruises.

There are concerns that the wind speed dependence of CO₂ exchange coefficient suggested by Liss and Merlivat (1986) may be underestimated at high wind speed. However, recent measurement in rough and stormy seas using a dual-tracer technique (Watson et al., 1991), and other studies of SF₆ budgeting in lakes (Upstill-Goddard et al., 1990) and in a wind-wave tank (Wanninkhof and Bliven, 1991) support gas transfer values estimated by the Liss-Merlivat relationship. Possible explanations for the higher gas exchange rate derived from ¹⁴C inventory method are given by Thomas et al. (1988) and Etcheto et al. (1991). Briefly, Thomas et al. (1988) suggested that the method using bomb-14C inventory relies mainly on the CO₂ invasion at high latitudes where gas transfer is relatively high, and thus, is not applicable to the global ocean. Etcheto et al. (1991) argued that the ¹⁴C inventory methods do not account fully for the distribution of natural ¹⁴C or the redistribution of bomb-¹⁴C in the interior of the ocean by ocean circulation.

The other uncertainty in CO₂ flux estimate concerns the wind speed data. Four different types of wind speed data have been used recently in estimating the CO₂ exchange coefficient, i.e., field measurements (Wong and Chan, 1991; Murphy

et al., 1991), wind climatologies (Tans et al., 1990; Murphy et al., 1991), wind field outputs from climate model (Thomas et al., 1988; Erickson, 1989), and satellite wind speed measurements (Etcheto and Merlivat, 1988; Etcheto et al., 1991). The last two types of data may be considered as derived or proxy data whose accuracy has to be assessed in more detail (e.g., Boutin and Etcheto, 1991). Data interpolated from monthly wind climatology may not be appropriate if eq. (1) is used to estimate air-sea CO₂ flux. Statistically, eq. (1) describes a dependency of the air-sea flux on K and ΔpCO_2 in which both the latter two parameters are correlated as functions of SST and salinity. However, when wind climatological data are used to estimate CO₂ exchange coefficients, the underlying assumption is that K and ΔpCO_2 are independent of one another. To satisfy this correlation, K and ΔpCO_2 necessarily have to be of about the same scales in both time and space, i.e., measure in the same general location and within hours or days. This requires practically that field measurements or satellite wind speed data be used in the $k_w - u_{10}$ relationship. This practice would retain also the assumed dependency of the Liss-Merlivat relationship since it is derived mainly from experiments for which the air-sea flux data are measured within a few days after the wind speed measurements.

Another uncertainty concerns the spatial and temporal variabilities in both the distribution of ΔpCO_2 and the wind speed used to estimate the CO₂ exchange coefficient. Studies which estimated the zonal net CO₂ flux using a single annual mean of ΔpCO₂ or CO₂ transfer velocity without taking into account the seasonal and regional variabilities of these parameters are subjected to errors (Thomas et al., 1988; Etcheto 'et al., 1991; Wanninkhof, 1992). The specific examples given by Etcheto and Merlivat (1988) show that errors as large as a factor of eight can arise if the variabilities are omitted. Since the $k_w - u_{10}$ or $K-u_{10}$ relationship is essentially nonlinear, the loss of much of the high frequency components in the climatological data would underestimate fluxes from high-latitude area where episodic strong winds are frequent and the seasonal ΔpCO₂ values differ widely (Etcheto and Merlivat, 1988; 1989) or would overestimate fluxes from certain equatorial regions where calm weather condition prevails for much of the time. Wanninkhof (1992) estimates the effect of wind speed distribution on estimating gas transfer velocity at a particular mean wind speed. His analysis suggests that gas transfer velocities measured over long time periods with variable winds will be higher than if gas transfer velocities are measured instantaneously or under steady wind conditions for the same average wind speed. Thus the Liss-Merlivat relationship will yield low gas transfer values if long-term averaged winds over the ocean are used. Conversely, the relationship used by Tans et al. (1990) will yield anomalously high values if used for short-term or steady winds (Wanninkhof, 1992).

6. Conclusions

During the 1987 El Niño, the oceanographic properties in surface seawater of the central equatorial Pacific showed an increase in SST accompanied by decreases in sea surface pCO₂ and \sum CO₂. At the same time, decreases of the dissolved nitrate, phosphate and silicate near the equatorial region were also recorded. These conditions, lasting for more than a year, appeared first during the August 1986 cruise and continued up to the September 1987 cruise. Observations from the December 1987 and the February 1988 cruises showed that the trends of the CO₂ system and the dissolved nutrients started to reverse as Pacific SST was cooling slowly.

The maximum reduction of Σ CO₂ supply to the surface layer by equatorial upwelling in September 1987 was estimated to be about 97–194 mM m⁻¹ d⁻¹. Similarly, the low replenishment of nitrate represented a maximum loss in new primary production of about 17–34 mM C m⁻² d⁻¹. For the non-El Niño condition from March 1985 to April 1986, the average CO₂ effluxes to the atmosphere from the central equatorial Pacific within the 5°S–5°N latitudinal band is estimated to be about 1.2 M CO₂ m⁻² yr⁻¹. During March 1987 to February 1988 when ENSO condition prevails, the evasion of CO₂ from the same oceanic region was reduced to about 0.2 M CO₂ m⁻² yr⁻¹.

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