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Geographical, seasonal and interannual variations of air-sea CO_2 exchange in the subtropical Pacific surface waters during 1983–1988

(II). Air-sea CO_2 fluxes with skin-temperature adjustments

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ABSTRACT

Air-sea fluxes of CO_2 in surface seawater of the northeast (15°N–45°N) and southwest (25°S–15°S) subtropical Pacific Ocean from January 1985 to February 1988 were estimated. Initially, the net CO_2 flux unadjusted for the temperature deviation at the sea surface microlayer was estimated as a multiplicative product of the CO_2 transfer velocity, the solubility of CO_2 in seawater, and the difference in CO_2 fugacities between surface seawater and air. The fugacities of CO_2 in surface seawater and in the overlying air were given in Part I of this report. We used the Liss-Merlivat formulation to estimate the CO_2 transfer velocity from wind speed and seawater temperature. The monthly mean CO_2 fluxes were also adjusted for the temperature deviation ΔT between the mixed layer and the surface skin. The mean ΔT was estimated from the climatological means of solar radiation and heat fluxes across the boundary layer. Estimated ΔT for 1985–1988 averaged about 0.3°C. The overall effect of the depressing skin temperature was an increased strength of the CO_2 sink, as expressed by a factor ϕ to estimate the surface temperature deviation on the net CO_2 flux for a given month and oceanic zone. The relative shifts between unadjusted and adjusted fluxes on a seasonal basis for each 10° latitudinal bands in the subtropical Pacific could vary between +56% and −71%. During the study period, the adjustments increased the net CO_2 fluxes within 25°S–15°S by 5% in austral winter and 56% in austral summer. Within 15°N–35°N, CO_2 effluxes reduced in the summer by 39% but increased in the winter by 15%. In northern waters within 35°N–45°N, the summer CO_2 effluxes were reduced by about 14%, whereas the winter CO_2 influxes showed an increased of about 7%. Thus, it is important to include the skin temperature effect in deriving the correct magnitude of the air-sea CO_2 flux. In the boreal winter/spring, the northeast Pacific within 15°N–35°N was a CO_2 sink with the adjusted net CO_2 flux averaged about −1.7 mmol CO_2 $m^{-2} d^{-1}$ during the 1986/1987 El Niño and about −2.2 mmol $m^{-2} d^{-1}$ before and after the El Niño. In the boreal summer/autumn, the CO_2 fluxes averaged respectively about 0.4 mmol $m^{-2} d^{-1}$ and 0.6 mmol $m^{-2} d^{-1}$ during the El Niño and the non-El Niño periods. Within 35°N–45°N, the average CO_2 flux was about 1.4 mmol $m^{-2} d^{-1}$ in summer; about −5.2 mmol $m^{-2} d^{-1}$ in the winter/spring. The southwest subtropical Pacific within 25°S–15°S was basically a CO_2 sink year round with net CO_2 flux averaged at about −2.0 mmol $m^{-2} d^{-1}$ in austral winter/spring and −0.7 mmol $m^{-2} d^{-1}$ in austral summer/autumn.

1. Introduction

The ocean plays an important role in the present-day global carbon cycle by absorbing a net amount of CO_2 from the air, and in effect, slows down the rising level of atmospheric CO_2. There is disagreement among estimates of the global oceanic uptake of CO_2. In general, the equatorial surface water is a CO_2 source while the North Atlantic Ocean and the vast oceanic area of

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the south temperate latitudes are CO_2 sinks (Takahashi et al., 1986; 1993; Takahashi, 1989; Tans et al., 1990). Tans et al. (1990), using an atmospheric general circulation model coupled with the oceanic distributions of wind speed and the difference in the partial pressures of CO_2 between the surface seawater and the overlying air (ΔpCO_2), estimate the global annual oceanic CO_2 sink to be less than 1.0 Gt C a^{-1}. This rate is about half of that obtained by an experimental approach based on $^{13}C/^{12}C$ (Quay et al., 1992) and by other simulation studies based on tracer-calibrated ocean models (Siegenthaler and Joos, 1992; Sarmiento et al., 1992; Stocker and Broecker, 1994). Recently, Sarmiento and Sundquist (1992) and Siegenthaler and Sarmiento (1993) after reviewing the major processes affecting the global CO_2 budget suggest a mean global oceanic CO_2 uptake rate of about 2 Gt C a^{-1}. Sarmiento and Sundquist (1992) also propose that the Tans et al. (1990) estimates may be revised upward by taking account of the effect of thermal skin temperature of the ocean mixed layer in calculating air-sea CO_2 fluxes.

The magnitude of CO_2 exchange between the ocean and the atmosphere is regulated by the CO_2 concentration gradient across the air-sea interface, the transfer resistance of CO_2 as a function of wind speed and molecular diffusivity, and the chemical reactivity and solubility of CO_2 in seawater. In practice, the concentration gradient of CO_2 across the air-sea interface is usually estimated by ΔpCO_2 as well as the corresponding CO_2 solubility in the mixed layer. However, the temperature and salinity of the upper 1 mm or so of sea surface deviate slightly from the bulk temperature and salinity measured for the mixed layer. Roos and Gravenhorst (1984) suggested the need to calculate different CO_2 solubilities for the two CO_2 concentration terms to account for the lower temperature and higher salinity at the skin or surface microlayer than that exist in the bulk seawater. The bulk-skin temperature deviation (ΔT) also implicates in estimating surface seawater pCO_2 (Smethie et al., 1985). An early effort to estimate the effect of skin temperature on CO_2 solubility (Robertson and Watson, 1992) uses the ΔT equation of Hasse (1971) to produce zonally averaged correction for air-sea CO_2 flux in June and December. This correction is cited by Sarmiento

Table 1. *The M/V Lillooet cruises*

Cruise no.	Dates	Notes
463N	10 Jan 1985–26 Jan 1985	route 2
465N	12 Mar 1985–29 Mar 1985	route 2
469N	12 Aug 1985–30 Aug 1985	no GC data south of 22°S; route 2
473N	16 Jan 1986– 2 Feb 1986	no GC data south of 20°S; route 4
475N	23 Mar 1986–13 Apr 1986	no GC data south of 17°S; route 2
479N	1 Aug 1986–19 Aug 1986	GC data for 21°S–2°N, 22–31°N; route 5
481N	11 Oct 1986–28 Oct 1986	no GC data north of 26°N; route 2
483N	14 Dec 1986– 2 Jan 1987	route 2
485N	21 Feb 1987–12 Mar 1987	route 2
487N	1 May 1987–26 May 1987	route 3
489N	21 Jul 1987–10 Aug 1987	no GC data south of 15°S; route 2
491N	20 Sep 1987– 8 Oct 1987	route 5
493N	26 Nov 1987–11 Dec 1987	route 6
494S	31 Dec 1987–12 Jan 1988	route 1
495N	4 Feb 1988–20 Feb 1988	route 6

route 1: Vancouver–Oakland–Sidney
route 2: Brisbane–Noumea–Suva–Honolulu–Vancouver
route 3: Brisbane–Noumea–Suva–Long Beach–Vancouver
route 4: Brisbane–Vancouver
route 5: Brisbane–Noumea–Suva–Honolulu–Oakland–Vancouver
route 6: Brisbane–Honolulu–Oakland–Vancouver.

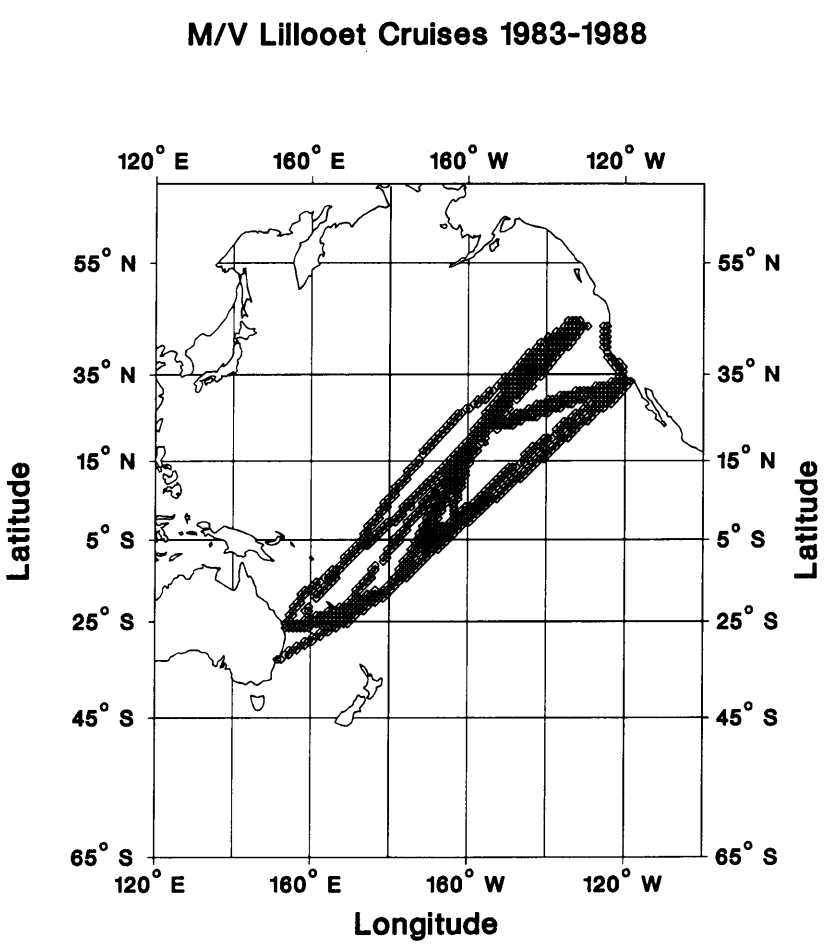

Fig. 1. Cruise tracks of M/V Lillooet.

and Sundquist (1992) as an important factor not accounted for by Tans et al. (1990) in their study of the oceanic uptake of CO_2.

The Centre for Ocean Climate Chemistry at the Institute of Ocean Sciences has measured fCO_2 of the Pacific Ocean during the Oceanic CO_2 Monitoring Project from November 1983 to February 1988 (Wong et al., 1984; 1993). This project is based on a ship-of-opportunity program and was carried out on board the German container-carrier *M/V Lillooet* which sailed between Canada and Australia 6 times a year. The nutrient levels and pCO_2 in surface seawater and net CO_2 fluxes near the central tropical Pacific during the 1986/1987 El Niño were reported earlier (Wong et al., 1993). Part I of the report (Wong et al., 1995) describes the geographical and temporal variations in the fugacity of CO_2 (fCO_2) in surface seawater of the subtropical and northeastern Pacific. In this Part II of the report, we present the results of net air-sea CO_2 flux during the 15 cruises between January 1985 and February 1988. Details of the cruises in 1985–1988 (Table 1) and a map of the cruise tracks (Fig. 1) were reproduced from Part I.

2. Method

The procedures for sampling and analyzing equilibrium CO_2 in surface seawater are described fully in Part I of this report and in Wong et al.

(1993). The method for computing CO_2 flux is also described in Wong and Chan (1991). In the following, we give only a description of the methodology for calculating CO_2 air-sea flux and other details relevant to this report. All the sampled data were screened for extreme outliers before averaging to obtain daily means. These were then averaged to obtain monthly or seasonal means. The boreal winter (or austral summer) season includes January and February of the current year plus December of the preceding year.

2.1. Net CO_2 flux

Procedure for calculating the net CO_2 flux without adjustment for the skin-temperature effect was given in our earlier reports (Wong and Chan, 1991; Wong et al., 1993). The net CO_2 flux, F, across the air-sea interface (Robertson and Watson, 1992) may be expressed by

$$F = k\{[CO_2^*] - [CO_2^s]\}, \quad (1)$$

where k is the CO_2 transfer velocity, and $[CO_2^*]$, $[CO_2^s]$ are, respectively, the concentrations of dissolved gaseous CO_2 at the base and the surface of the diffusion-dominated microlayer at the air-sea interface. In practice, the in situ CO_2 flux is usually approximated by

$$F = ks(fCO_{2w} - fCO_{2a}) \quad (2)$$

(Smethie et al., 1985; Wong and Chan, 1991; Wong et al., 1993, Wanninkhof and Thoning, 1993), where s is the solubility of CO_2 in seawater (Weiss, 1974) calculated at the temperature and salinity of the bulk mixed layer, and fCO_{2w}, fCO_{2a} are, respectively, the fugacities of CO_2 in equilibrium with seawater of the mixed layer and in the overlying air. Results of fCO_{2a} and fCO_{2w} from our cruises were reported in Part I (Wong et al., 1995). Note that eqs. (1)–(2) differ slightly from those given by Robertson and Watson (1992) in having the two fugacity terms in reverse order to be consistent with other studies of CO_2 air-sea exchange. In eq. (2), the CO_2 solubilities at the sea surface and of the bulk mixed layer are assumed to be equal.

The CO_2 transfer velocity, k (cm h^{-1}), was estimated from wind speed at 10-m height for three different wind regimes using the Liss-Merlivat formulation (Andrié et al., 1986; Liss and Merlivat, 1986; Liss, 1988), i.e.,

$$k = 0.17u_{10}(Sc_{20}/Sc)^{2/3}, \quad \text{for} \quad u_{10} \leqslant 3.6, \quad (3a)$$

$$k = [2.85u_{10} - 9.65](Sc_{20}/Sc)^{1/2}, \quad \text{for} \quad 3.6 < u_{10} \leqslant 13, \quad (3b)$$

$$k = [5.9u_{10} - 49.3](Sc_{20}/Sc)^{1/2}, \quad \text{for} \quad u_{10} > 13, \quad (3c)$$

where u_{10} is the wind speed (m s^{-1}) at 10-m height, and Sc_{20}, Sc are, respectively, the Schmidt numbers at 20°C and at the SST. A third-order polynomial equation given by Wanninkhof (1992) was used to estimate the Schmidt number for CO_2 at a given temperature. The solubility of CO_2 in seawater at the temperature and salinity of the bulk mixed layer was estimated according to the equation of Weiss (1974). The product ks, which is a convenient parameter to describe the state of the sea surface, is referred to as the CO_2 exchange coefficient K (Etcheto and Merlivat, 1988; Heimann and Monfray, 1989). Any chemical enhancement to the CO_2 air-sea gas exchange was assumed to be negligible (Goldman and Dennett, 1983). However, from theoretical consideration, Wanninkhof (1992) estimated that at an average wind speed of 4.7 m s^{-1} there is a 6% chemical enhancement using the Liss-Merlivat formulation.

During cruises 489N to 495N, wind speed at 1° latitude interval were recorded. For these cruises, the observed wind speeds 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 that were observed within a 50 km radius from the track and less than three hours before the time of the CO_2 measurements. If more than one value was found, we used the one nearest to the exact location of the cruise track.

2.2. Deviation of sea surface temperature

The temperature at the top 1 mm or so of the sea surface (the "skin" or the microlayer) may deviate slightly from the seawater temperature measured

in the bulk mixed layer or at the intake of the equilibrator because of radiative, evaporative and conductive heat flows at the air-sea interface. Since the solubility of CO_2 in seawater is a strong function of temperature, the solubility at the skin of the mixed layer would differ from the solubility calculated for the bulk mixed layer. Estimates of the bulk-skin temperature deviation ΔT are essential to assess the effect of different solubility values in marine CO_2 flux estimations. This temperature deviation is usually associated with the local energy fluxes through the aqueous microlayer (Hasse, 1971; Grassl, 1976; Schluessel, 1990). An equation to correct for a slight deviation in skin temperature from SST measured at 5 m below sea surface is given by Hasse (1971) as

$$\Delta T = T_0 - T_w = 10.5(H/u) + 2.32(Q/u), \quad (4)$$

where T_0 is the skin temperature (°C), T_w is the mixed-layer temperature (°C), u is the local wind speed ($m\,s^{-1}$), Q is the incident solar radiation ($ly\,min^{-1}$), and H is the heat flow at the surface ($ly\,min^{-1}$) which is the sum of effective upward longwave radiation plus latent and sensible heat transfer to the atmosphere. Hasse (1971) also provided separate values of the 2 coefficients in the equation for other reference depths where T_w are taken. In eq. (4), downward radiative flux is defined as positive, and upward heat flow, negative; so ΔT is usually negative.

Since no heat-budget data were observed during our cruises, adjustment for the effect of skin temperature was not made on the individual in situ flux estimate. However, the magnitude of this effect might be estimated with eq. (4) by using the monthly means of SST and wind speed from our cruises and the climatological month means of solar radiation and heat fluxes over the oceanic region crossed by the *Lillooet's* cruise tracks. The monthly means of Q and H for each latitudinal zone were estimated from the climatological means of oceanic heat budget compiled by Esbensen and Kushnir (1981). The $4° \times 5°$ grid values of monthly solar radiation, F_s ($W\,m^{-2}$), and heat fluxes, $F_I + F_H + F_{LE}$ ($W\,m^{-2}$), given by Esbensen and Kushnir (1981) within the 4 latitudinal zones of 25°S–15°S, 15°N–25°N, 25°N–35°N and 35°N–45°N were averaged to obtain the mean values for these zones. All averages of heat fluxes were converted to the proper unit.

2.3. *CO_2 flux adjusted for bulk-skin temperature difference*

To adjust the estimate of CO_2 flux for a bulk-skin temperature deviation in the mixed layer, the CO_2 solubility at the microlayer of the air-sea interface should be calculated at the skin temperature T_0 and the surface salinity. In our study, we assumed that changes in the surface salinity would be negligible, and so, substituted the mixed layer salinity for the surface salinity. Since only monthly mean ΔT was estimated, the adjustment was applied only to the monthly averages in CO_2 flux calculation. In the following, we shall use an overbar to denote the mean value of observations or estimates averaged over a given month for a given zone and an asterisk to denote an estimate derived from these monthly means such as the monthly mean of bulk-skin temperature deviation, ΔT^* (Table 2). Likewise, the monthly mean solubility of CO_2 in the bulk mixed layer (s_w^*) was calculated by using the monthly means of SST and salinity of the mixed layer, and the mean solubility of CO_2 at the ocean surface (s_0^*) was computed from the means of skin temperature and surface salinity.

Using the monthly means of transfer velocity and solubility of CO_2 in the bulk mixed layer, the unadjusted mean CO_2 flux could be estimated as

$$F_n^* = \bar{k}[\overline{s_w}\,\overline{fCO_{2w}} - \overline{s_w}\,\overline{fCO_{2a}}] = \bar{k}\overline{s_w}[\overline{\Delta fCO_2}]. \quad (5)$$

Following Robertson and Watson (1992), we could then set the CO_2 solubility at the skin temperature and salinity as

$$s_0^* = (1+\delta)\, s_w^*, \quad (6)$$

and assuming that

$$\delta = \frac{s_0^* - s_w^*}{s_w^*} \approx \frac{\overline{s_0} - \overline{s_w}}{\overline{s_w}}. \quad (7)$$

It followed that the equation for the adjusted mean CO_2 flux becomes

$$F_a^* = \bar{k}[\overline{s_w}\,\overline{fCO_{2w}} - \overline{s_0}\,\overline{fCO_{2a}}] = \bar{k}[\overline{s_w}\,\overline{fCO_{2w}} - (1+\delta)\,\overline{s_w}\,\overline{fCO_{2a}}], \quad (8a)$$

Table 2. *Monthly mean bulk-skin temperature deviation (ΔT^*) and CO_2 flux*

Cruise	Date (yy/mm)	ΔT^* (°C)	Wind speed ($m\,s^{-1}$)	CO_2 transfer velocity ($cm\,h^{-1}$)	δ [eq. (7)][$] (%)	Adjustment factor ϕ [eq. (9)]	$\overline{F_n}$[#] ($mmole\,m^{-2}d^{-1}$)	$\overline{F_a}$[@] ($mmole\,m^{-2}d^{-1}$)
25–15°S								
463N	85/01	−0.22	8.5	24.3	0.53	1.37	−0.50	−0.68
465N	85/03	−0.25	8.1	17.8	0.61	1.13	−0.75	−0.83
469N	85/08	−0.28	8.9	17.9	0.73	1.06	−5.53	−5.84
473N	86/01	−0.17	11.1	34.1	0.40	0.66	1.40	0.92
475N	86/03	−0.29	7.1	13.8	0.70	1.15	−0.70	−0.81
479N	86/08	−0.41	6.1	9.8	1.07	1.08	−2.70	−2.93
481N	86/10	−0.39	4.8	5.1	0.99	1.14	−0.78	−0.89
483N	86/12	−0.23	6.9	13.5	0.57	1.16	−0.68	−0.79
485N	87/02	−0.23	7.9	17.7	0.55	1.14	−1.12	−1.27
487N	87/05	−0.31	8.8	20.8	0.78	1.12	−2.15	−2.41
489N	87/07	−0.62	4.6	6.3	1.65	1.75	0.14	0.24
491N	87/09	−0.33	6.7	13.0	0.88	1.10	−2.40	−2.63
493N	87/11	−0.23	7.2	13.5	0.58	1.32	−0.05	−0.07
494S	88/01	−0.27	6.9	19.5	0.66	0.56	−0.85	−0.48
495N	88/02	−0.31	5.7	8.3	0.75	0.59	0.45	0.26
15–25°N								
463N	85/01	−0.21	8.9	20.1	0.54	1.17	−1.21	−1.42
465N	85/03	−0.20	10.1	24.2	0.52	1.08	−3.15	−3.39
469N	85/08	−0.53	4.6	5.8	1.33	0.32	0.52	0.16
473N	86/01	−0.18	10.6	29.5	0.45	1.08	−2.64	−2.85
475N	86/04	−0.29	8.4	16.8	0.75	1.24	−0.75	−0.93
479N	86/08	−0.25	9.7	20.8	0.64	0.62	1.51	0.94
481N	86/10	−0.23	7.9	18.1	0.56	0.77	1.57	1.21
483N	86/12	−0.18	8.7	19.6	0.46	1.09	−1.87	−2.04
485N	87/03	−0.28	7.4	13.5	0.73	1.09	−2.32	−2.52
487N	87/05	−0.42	6.6	10.6	1.09	1.37	−0.52	−0.72
489N	87/08	−0.50	4.9	8.9	1.24	0.59	0.76	0.45
491N	87/10	−0.28	6.6	11.7	0.68	0.52	0.79	0.41
493N	87/12	−0.17	9.1	21.1	0.44	1.21	−0.48	−0.58
494S	88/01	−0.58	3.2	3.9	1.53	1.27	−0.64	−0.81
495N	88/02	−0.22	8.1	15.2	0.56	1.54	−0.05	−0.08
25–35°N								
463N	85/01	−0.24	7.7	14.9	0.67	1.14	−2.19	−2.48
465N	85/03	−0.25	8.2	14.8	0.70	1.06	−3.94	−4.20
469N	85/08	−0.33	7.5	13.7	0.86	0.24	0.49	0.12
473N	86/01	−0.28	6.6	12.1	0.79	1.08	−3.36	−3.62
475N	86/04	−0.28	8.7	16.6	0.82	1.08	−4.71	−5.10
479N	86/08	−0.43	5.8	8.4	1.14	0.67	1.96	0.65
481N	86/10	−0.28	6.5	10.4	0.75	0.70	1.05	0.74
483N	86/12	−0.16	10.0	21.9	0.44	1.06	−4.15	−4.40
485N	87/03	−0.31	6.6	9.7	0.92	1.08	−3.20	−3.47
487N	87/05	−0.41	6.6	9.7	1.19	1.70	−0.39	−0.67
489N	87/08	−0.41	6.0	9.1	1.07	0.81	1.34	1.09
491N	87/10	−0.34	5.4	7.8	0.91	−1.73	0.22	−0.38
493N	87/12	−0.18	8.9	18.7	0.49	0.70	1.41	0.99
494S	88/01	−0.50	3.7	2.5	1.44	1.28	−0.37	−0.47
495N	88/02	−0.16	11.4	22.9	0.45	1.33	−0.51	−0.67
35–45°N								
463N	85/01	−0.38	4.8	4.5	1.15	1.13	−1.43	−1.62
465N	85/03	−0.22	9.3	15.8	0.67	1.07	−5.35	−5.70
469N	85/08	−0.30	8.2	20.2	0.86	0.68	0.17	0.17
473N	86/01	−0.16	11.4	25.0	0.51	1.07	−6.27	−6.70
475N	86/04	−0.28	8.8	12.9	0.89	1.08	−4.90	−5.27
483N	86/12	−0.15	11.2	25.3	0.48	1.08	−5.65	−6.02
485N	87/03	−0.25	8.1	12.4	0.81	1.08	−4.39	−4.75
489N	87/08	−0.31	8.0	13.4	0.91	0.88	3.02	2.64

[$] Fractional increase of CO_2 solubility at skin temperature relative to solubility at bulk temperature.
[#] Monthly means of CO_2 flux unadjusted for skin-temperature effect.
[@] Monthly means of adjusted CO_2 flux.

or, rearranged the terms to express as

$$F_a^* = \bar{ks}_w[\overline{\Delta fCO_2} - \delta(\overline{fCO_{2a}})]. \quad (8b)$$

The correction factor,

$$\phi = F_a^*/F_n^*, \quad (9)$$

could provide an estimate of the effect of skin-temperature deviation on net CO_2 flux for a given month and oceanic zone.

3. Results and discussion

The southwest and northeast subtropical regions are conveniently divided as in Part I (Wong et al., 1995) into several latitudinal zones: 25° S–15° S, 15° N–25° N, 25° N–35° N and 35° N–45° N. Figs. 2–5 show both the daily and seasonal averages of CO_2 transfer velocity, CO_2 solubility at in situ seawater salinity and tem-

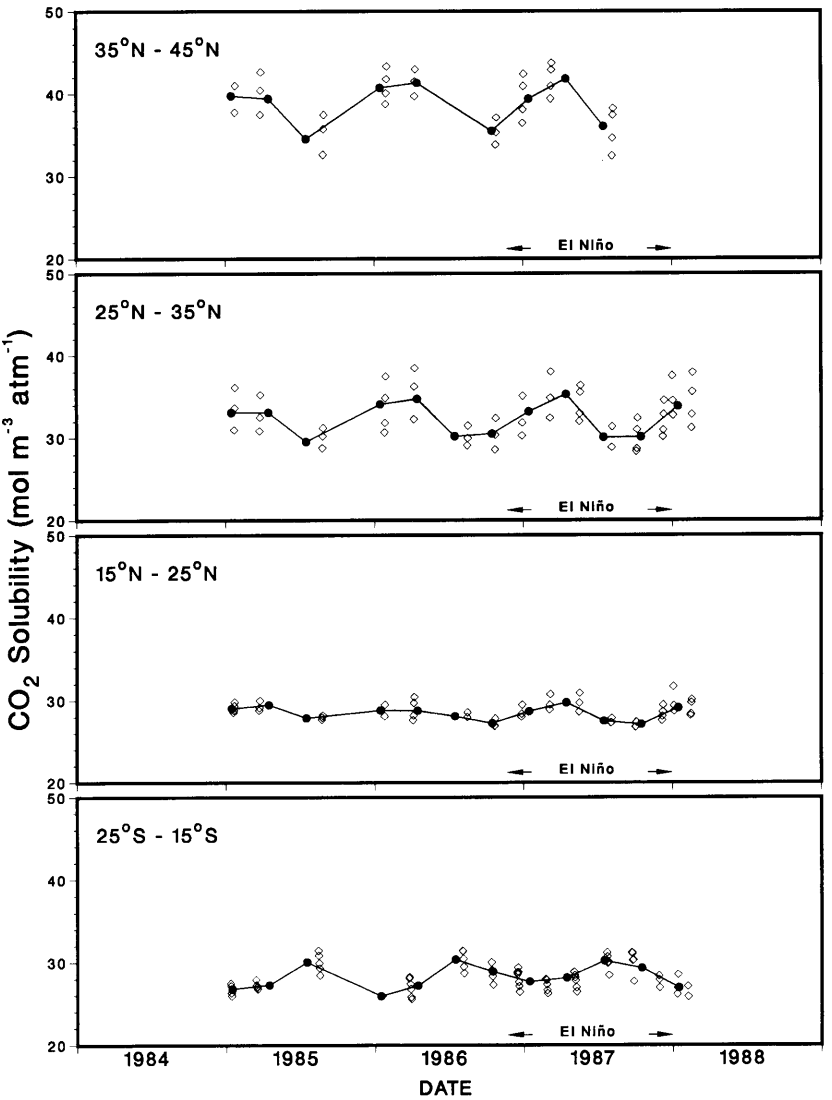

Fig. 2. Monthly average of CO_2 solubility (mol m^{-3} atm^{-1}) in the mixed layer for the southwest and northeast Pacific between January 1985 and February 1988. The daily means are shown as diamonds; the seasonal means (solid dots) are connected by straight line. The boreal winter (austral summer) season includes January and February of the current year plus December of the preceding year.

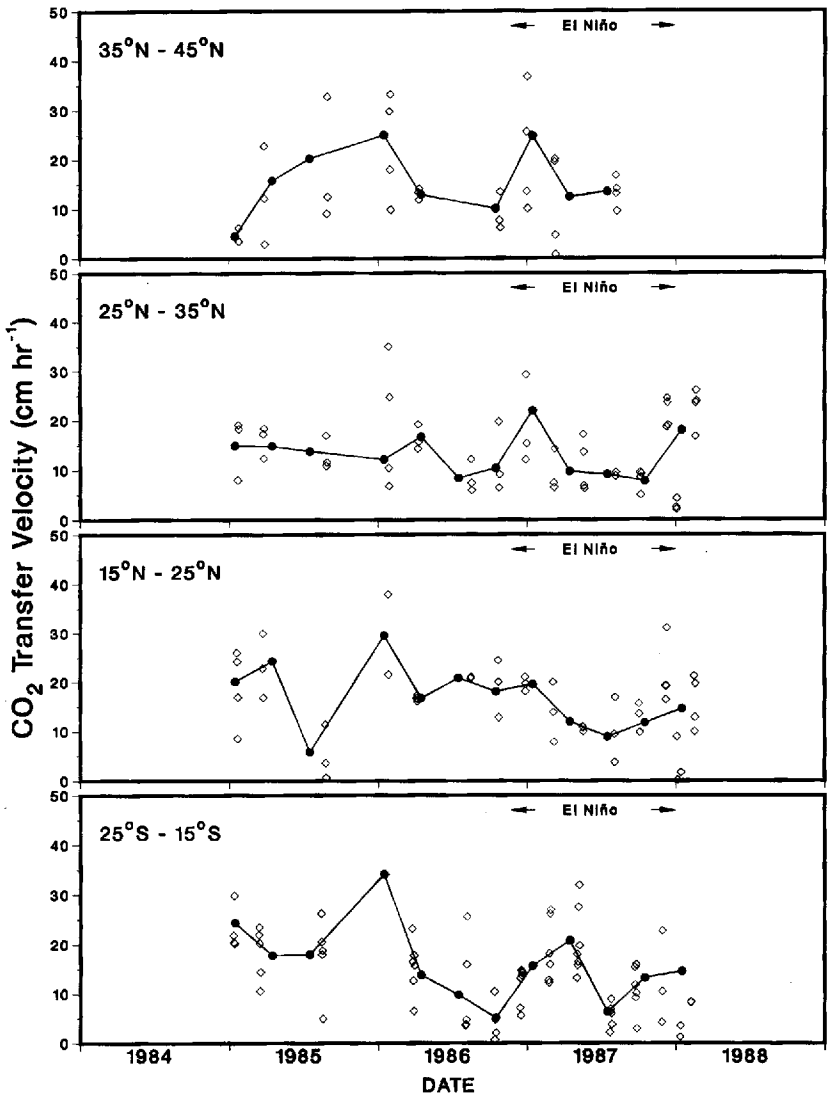

Fig. 3. Monthly average of CO_2 transfer velocity (cm h^{-1}) for the southwest and northeast Pacific between January 1985 and February 1988. The diamond-shaped points are daily means; the solid dots connected by straight line are seasonal means.

perature, CO_2 exchange coefficient, and the net CO_2 flux respectively. Table 2 gives the monthly means of the temperature deviation ΔT^*, δ (in eq. (7)), the adjustment factors ϕ (in eq. (9)), the unadjusted CO_2 fluxes $\overline{F_n}$ from each cruise within a given zone, and the adjusted CO_2 flux $\overline{F_a}$ as the product of $\phi \times \overline{F_n}$.

3.1. Bulk-skin temperature deviation

The bulk-skin temperature deviations, ΔT^* (Table 2), were estimated from the monthly means of SST, salinity, solar radiation and heat flux through the microlayer. During 1985–1988, the values of ΔT^* ranged from -0.14°C in January

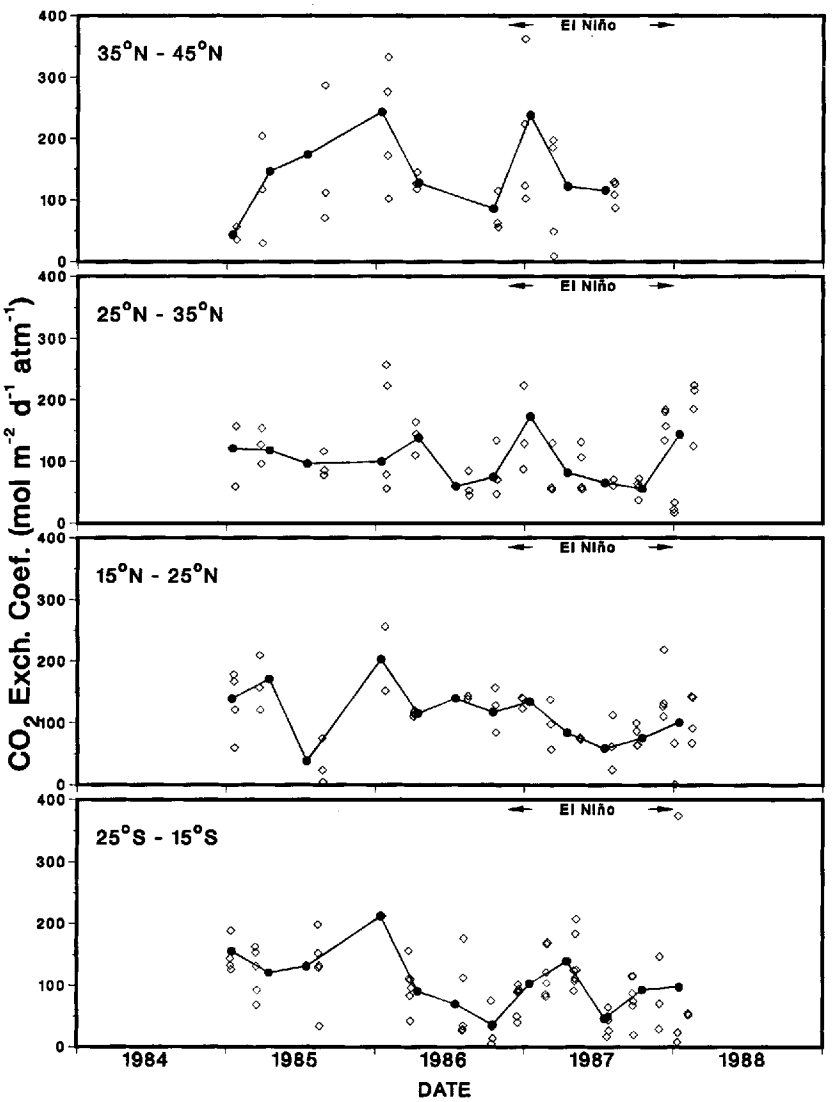

Fig. 4. Monthly average of CO_2 exchange coefficient (mol m^{-2} d^{-1} atm^{-1}) for the southwest and northeast Pacific between January 1985 and February 1988. The diamond-shaped points are daily means; the solid dots connected by straight line are seasonal means.

1987 to −0.62°C in July 1987. Within 25°S–15°S and 15°N–25°N, the ΔT^* in July–August averaged about 0.2°C lower than that in December–February. In the northeast Pacific, the magnitudes of ΔT^* in both winter and summer decreased from 15°N–25°N to 35°N–45°N. Along the cruise tracks of the *M/V Lillooet*, the overall average ΔT during the study period was about −0.3°C.

Values of ΔT^* calculated from the monthly means of wind speed, solar radiation and heat flux as in this report probably differ from the values obtained by direct averaging of ΔT values calculated from in situ observations. The difference is not easy to estimate because of the nonlinearity of eq. (4). However, the error caused by using ΔT^* in our analysis could be minimized by applying the

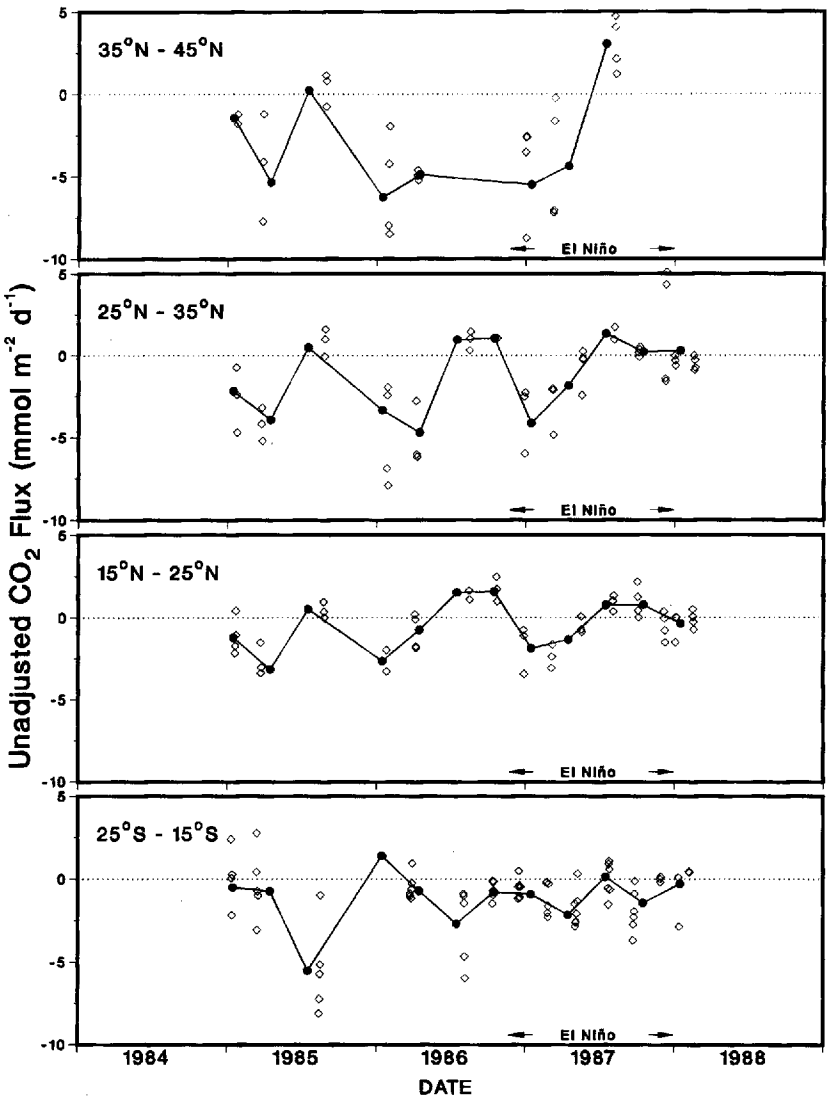

Fig. 5. Monthly average of net CO_2 flux (mmol m^{-2} d^{-1}) for the southwest and northeast Pacific between January 1985 and February 1988. The fluxes are unadjusted for the skin-temperature effect. The diamond-shaped points are daily means; the solid dots connected by straight line are seasonal means.

skin-temperature adjustment only to the monthly means of CO_2 flux. Possible errors in computing annual mean of CO_2 flux using either zonally and seasonal means of CO_2 exchange coefficient and ΔfCO_2 were discussed by Thomas et al. (1988). One of their examples showed that when the products of K and ΔpCO_2 are averaged zonally and seasonally, the result is a factor of 6 larger than the result when the averages are made on the two terms separately, befor making the product.

Besides the Hasse (1971) formula, other formulations of ΔT were also suggested by Saunders (1967) and Schluessel et al. (1990). Schluessel et al. (1990) proposed separate ΔT equations for day and for night observations based on their radiometric measurements of skin temperature in the

North Atlantic Ocean. They found that, on the average, the skin temperature was 0.11°C cooler than the bulk temperature at day, and 0.3°C cooler at night. Smethie et al. (1985) estimated ΔT values for the tropical Atlantic TTO/TAS stations in 1982–1983 using climatological means of wind speed and heat flux with the equation of Saunders (1967). The ΔT for tropical Atlantic averaged about −0.21°C, corresponding to a reduction of surface seawater fCO_2 by about 1% (or 3 to 4 μatm). An early study on the implications of skin temperature for CO_2 uptake (Robertson and Watson, 1992) estimated the global average ΔT for June and December with the Hasse (1971) equation using also the climatological means of wind speed, solar radiation and oceanic heat flux. These results showed that globally the ocean surface is generally cooler than the mixed layer by about 0.3°C. By applying the ΔT correction in CO_2 flux calculation, Robertson and Watson (1992) estimated that the ocean would produce an increased CO_2 uptake of 0.7 Gt C a^{-1}. Sarmiento and Sundquist (1992), in revising the budget for the oceanic uptake of CO_2, estimate that the effect of the cooler skin temperature is to give an increase in the average ΔpCO_2 estimates of about 1.1–4.3 ppm. Also, this increase in ΔpCO_2, if apply over the entire globe, would give an increased flux of 0.1–0.6 Gt C a^{-1} into the ocean.

Our ΔT^* results estimated for the three zones of the northeastern Pacific in December averaged about −0.17°C (Table 2). This value was less than the −0.25°C to −0.45°C obtained by Robertson and Watson (1992). Although we also employed the equation by Hasse (1971), both sets of results would differ because of differences in two respects. Firstly, Robertson and Watson (1992) used the coefficients intended for bulk temperature measured at 2.5 m depth, while we recorded mixed layer temperature at 5 m depth and replaced the equation with the appropriate coefficients accordingly. Secondly, different sets of climatological mean values were used in Robertson and Watson (1992) and our studies.

3.2. *Solubility of CO_2 in bulk mixed layer*

The solubilities of CO_2 in the mixed layer within 25°S–15°S and 15°N–25°N averaged about 29.5 ± 1 mol m^{-3} atm^{-1} in winter and decreased to 27.4 ± 0.7 mol m^{-3} atm^{-1} in summer. Within 25°N–35°N, the average CO_2 solubility was about 33.7 ± 2.3 mol m^{-3} atm^{-1} in winter but decreased slightly to 29.9 ± 1.2 mol m^{-3} atm^{-1} in summer. The averages increased within 35°N–45°N in both winter and summer to 40.1 ± 1.8 mol m^{-3} atm^{-1} and 35.3 ± 2.0 mol m^{-3} atm^{-1} respectively (Fig. 2).

In our analyses, the effect of ΔT on the solubility of CO_2 could be estimated from eq. (7) where δ represents the fractional increase in CO_2 solubility at bulk temperature relative to the solubility at the skin temperature. In general, the CO_2 solubility of the surface microlayer was about 0.8% higher than the solubility estimated for the bulk mixed layer. Hence the effect of skin temperature was to give a small increase of about 3 μatm in the average ΔfCO_2 term given in eq. (8) by assuming an atmospheric fCO_2 of about 340 μatm.

3.3. *CO_2 transfer velocity and exchange coefficient*

The CO_2 transfer velocity estimated for 25°S–15°S averaged about 12 ± 11 cm h^{-1} in austral winter and increased to about 18 ± 25 cm h^{-1} in austral summer. For the northeast Pacific within 15°N–35°N, the winter averages of 18 ± 18 cm h^{-1} decreased to a summer average of 10 ± 10 cm h^{-1}. Averages estimated for zone 35°N–45°N were higher: 20 ± 25 cm h^{-1} in the winter and 17 ± 34 cm h^{-1} in the summer (Fig. 3).

The transfer velocities of radon determined for GEOSECS Pacific at station 212 (30.0°N, 159.8°W) in September 1973 with wind speed of 6.4 m s^{-1} and station 233 (18.2°N, 169.1°W) in November 1973 with wind speed of 9.6 m s^{-1} averaged about 2.1 m d^{-1} (Peng et al., 1979). This average was equivalent to about 11 cm h^{-1} for CO_2 by assuming a Schmidt number dependency of −0.5. From our cruise 481N (October 1986) and cruise 491N (October 1987), the CO_2 transfer velocities for 15°N–45°N averaged about 12.8 cm h^{-1} with wind speed of 7.1 m s^{-1} and 9.8 cm h^{-1} with wind speed of 6.0 m s^{-1} respectively. Both the averages from our cruises and the GEOSECS radon measurements were therefore comparable.

The CO_2 exchange coefficient is primarily a function of wind speed since the effects of temperature on the CO_2 transfer velocity and on CO_2 solubility nearly cancel one another (Etcheto and Merlivat, 1988). Thus the estimated CO_2 exchange coefficients were as varied as surface wind speeds. In the southern zone 25°S–15°S, the estimated exchange coefficient for austral summer aver-

aged 115 ± 160 mol CO_2 m^{-2} d^{-1} atm^{-1} (Fig. 4). During 5–6 February 1988 (Cruise 495°N), the average exchange coefficient calculated for this area was 53 mol m^{-2} d^{-1} atm^{-1} (or 1.9×10^{-2} mol m^{-2} a^{-1} μatm^{-1}). This value was smaller than $2.9–4.4 \times 10^{-2}$ mol m^{-2} a^{-1} μatm^{-1} for the whole month of February estimated by Etcheto et al. (1991). In austral winter, the average CO_2 exchange coefficient estimated for this zone decreased to 85 ± 83 mol m^{-2} d^{-1} atm^{-1} (Fig. 4).

Within 15°N–35°N, the average CO_2 exchange coefficients in boreal winter and summer were about 132 ± 125 mol m^{-2} d^{-1} atm^{-1} and 71 ± 66 mol m^{-2} d^{-1} atm^{-1} respectively. The averages in northern waters within 35°N–45°N increased to 192 ± 249 mol m^{-2} d^{-1} atm^{-1} in boreal winter and 145 ± 301 mol m^{-2} d^{-1} atm^{-1} in boreal summer (Fig. 4). The contour of CO_2 exchange coefficient for February 1988 given by Etcheto et al. (1991) may be compared with the results from Cruise 495N. For examples, the average CO_2 exchange coefficient between 13–16 February 1988 for 15°N–25°N was 106 mol m^{-2} d^{-1} atm^{-1} (3.9×10^{-2} mol m^{-2} a^{-1} μatm^{-1}) and was within the range of $2.9–4.4 \times 10^{-2}$ mol m^{-2} a^{-1} μatm^{-1} for the February average given by Etcheto et al. (1991). However, the average for zone 25°N–35°N between 16–19 February 1988 of 190 mol m^{-2} d^{-1} atm^{-1} (6.9×10^{-2} mol m^{-2} a^{-1} μatm^{-1}) was higher than the range of $1.5–2.9 \times 10^{-2}$ mol m^{-2} a^{-1} μatm^{-1} from the same February average given by Etcheto et al. (1991).

Our estimates of the CO_2 transfer velocity relied on the Liss-Merlivat formulation (eq. (3)) which is derived mainly from data of radon deficit in lake and wind tunnel experiments (Liss and Merlivat, 1986; Liss, 1988). The means of CO_2 transfer velocity were in general agreement with values given in the global maps estimated by Thomas et al. (1988) and Erickson (1989). Both of them also estimated the transfer velocity fields from the Liss-Merlivat formulation. Their area-weighted yearly means of 10–12 cm h^{-1} were about half the mean value of 20 cm h^{-1} deduced from natural and bomb-produced ^{14}C decay model (Broecker et al., 1986).

One of the uncertainties in estimating air-sea flux of CO_2 is the value chosen for the transfer velocity. Wanninkhof (1992) has reviewed the experimental and field measurements of transfer velocity and the $k - u_{10}$ relationships proposed by previous studies. His compilation shows that, most of the gas transfer relationships are within the envelop of a strong-dependency equation proposed by Smethie et al. (1985) and a weak-dependency equation by Hartman and Hammond (1985). In recent years, the Liss-Merlivat gas transfer relationship was also supported by field studies (Upstill-Goddard et al., 1990; Wanninkhof and Bliven, 1991; Watson et al., 1991). However, several different approaches including a field experiment (Wanninkhof et al., 1993), the inference from nodel simulations (Sarmiento et al., 1992), and the results from a different formulation emphasizing the contributions from oceanic whitecaps (Erickson, 1993), all suggest higher global averages of CO_2 transfer velocity as given by the Liss-Merlivat formulation. Tans et al. (1990) used an empirical formulation based on wind tunnel data calibrated by global ^{14}C inventories to describe the relationship between the CO_2 exchange coefficient and wind speed. In this report, we did not use the equations of Tans et al. (1990) to estimate the in situ values of CO_2 exchange coefficient since their equations are more suitable to estimate the exchange coefficient with long-term wind (Murphy et al., 1991; Wanninkhof, 1992; Wong et al., 1993). Furthermore, these equations would required some modification to take into account the effects of local and short-term variabilities, such as a depressed skin temperature, oceanic bubble distribution, etc., on CO_2 flux.

3.4. *Net CO_2 flux unadjusted for ΔT*

Between January 1985 and February 1988, the southwest Pacific within the zonal belt 25°S–15°S was a net CO_2 sink annually. In the northeast Pacific, the ocean was a CO_2 source in boreal summer/autumn but a larger CO_2 sink in boreal winter/spring (Fig. 5). The averages of unadjusted CO_2 fluxes for austral autumn within 25°S–15°S (Table 3), especially the value for May 1987, may be compared with the results of Murphy et al. (1991) who also collected seawater fCO_2 data around this region at about the same time. In May 1987, the estimated net CO_2 flux from our cruise 487N within 25°S–15°S was -2.1 mmol m^{-2} d^{-1}, while the unadjusted fluxes from the cruises in March of 1985 and 1986 averaged about -0.7 mmol m^{-2} d^{-1} (or -0.3 mol m^{-2} a^{-1}). The latter value was slightly higher than the range of 0 to -0.2 mol m^{-2} a^{-1} for the same general

Table 3. *Summary of the seasonal and annual means of CO_2 fluxes*

	$\bar{K}$ (mole $m^{-2} a^{-1} \mu atm^{-1}$)	$\overline{\Delta fCO_2}$ (μatm)	$\overline{F_n}$ (mole $m^{-2} a^{-1}$)	$\overline{F_a}$ (mole $m^{-2} a^{-1}$)	Rel. inc. (%)
(1)	(2)	(3)	(4)	(5)	(6)
25°S–15°S					
summer	0.046	−5.23	−0.08	−0.12	56
autumn	0.043	−17.37	−0.44	−0.49	13
winter	0.030	−32.26	−0.99	−1.04	5
spring	0.027	−20.13	−0.39	−0.44	11
year	0.036	−18.75	−0.47	−0.52	
15°N–25°N					
winter	0.046	−14.33	−0.42	−0.47	13
spring	0.042	−18.06	−0.62	−0.69	12
summer	0.029	1.92	0.34	0.19	−44
autumn	0.035	6.40	0.43	0.29	−31
year	0.038	−6.02	−0.07	−0.17	
25°N–35°N					
winter	0.046	−15.05	−0.56	−0.65	16
spring	0.038	−28.56	−1.12	−1.23	10
summer	0.027	11.53	0.34	0.23	−34
autumn	0.024	4.78	0.23	0.07	−71
year	0.034	−6.82	−0.28	−0.40	
35°N–45°N					
winter	0.071	−24.90	−1.73	−1.86	7
spring	0.048	−35.91	−1.78	−1.91	7
summer	0.053	16.90	0.60	0.51	−14
year	0.056	−6.75	−0.58	−0.69	

The columns are seasonal or annual means of observations averaged over the appropriate period for: (2) CO_2 exchange coefficient, (3) ΔfCO_2, (4) unadjusted CO_2 flux, (5) CO_2 flux adjusted for skin-temperature effect, and (6) relative increase of columns 4 and 5 calculated as $100\% \times (F_a - F_n)/F_n$.

location given in the contour map of CO_2 flux by Murphy et al. (1991). Their results were obtained by using the 150-year climatological wind field and the equations for exchange coefficient by Tans et al. (1990). Since the ΔfCO_2 values from Murphy et al. (1991) and our cruises were comparable (Wong et al., 1995), the discrepancy in the flux results might stem mainly from the uses of different values of wind-field data and the CO_2 exchange coefficient.

3.5. *Adjusted net CO_2 flux for ΔT*

Table 2 gives the adjustment factors ϕ for the skin temperature on monthly mean CO_2 fluxes. In the northern Pacific, the values of ϕ generally decreased from south to north. This trend was reversed in the summer of 1987 during the El Niño period. Although the values of ϕ ranged from −1.7 to 1.8, most of these values were within the narrower range of 0.6–1.4. About two-third of the ϕ values were greater than 1 which mainly applied to CO_2 influxes (negative values). The other adjustment factors with values less than 1 occurred mainly in the summer hemisphere and applied mostly to CO_2 effluxes (positive values). There was one negative ϕ value which occurred when the averaged ΔfCO_2 has a small positive value but less than the adjustment from the skin-temperature effect.

The adjusted net CO_2 fluxes $\overline{F_a}$ (Table 2) were obtained by multiplying the corresponding adjustment factors with the monthly mean fluxes $\overline{F_n}$ calculated from the in situ measurements. Within 25°S–15°S, the net CO_2 flux averaged about -2.0 mmol $m^{-2} d^{-1}$ in austral winter/spring but reduced to about -0.7 mmol $m^{-2} d^{-1}$ in austral summer/autumn (Fig. 5). In the North Pacific, the variabilities of the CO_2 fluxes reflected those of

ΔfCO_2 (Wong et al., 1995). Our results showed bascially CO_2 influxes in boreal winter/spring but CO_2 effluxes in boreal summer/autumn with the magnitude of influxes generally larger than that of effluxes. Furthermore, both influxes and effluxes also increased poleward (Table 3). For the northeast Pacific within 15°N–35°N, the net CO_2 fluxes in boreal summer/autumn during the study period averaged about 0.5 mmol $m^{-2} d^{-1}$, while in boreal winter/spring, the average net flux was about -2.0 mmol $m^{-2} d^{-1}$. In northern waters within 35°N–45°N, the averaged net fluxes in summer/autumn and winter were about 1.4 and -5.2 mmol CO_2 $m^{-2} d^{-1}$ respectively.

As mentioned earlier, the adjustment factors applied to CO_2 influxes were mainly greater than 1 but were mostly less than 1 for effluxes. On a yearly basis, the net effect thus depended on the relative size of the adjustment for each season. In Table 3, columns 4 and 5 list the seasonal and yearly means of unadjusted and adjusted CO_2 fluxes respectively from our studies. Within 25°S–15°S, the adjustments increased the net CO_2 fluxes by 5% in austral winter and 56% in austral summer. Within 15°N–35°N, the adjustments reduced CO_2 effluxes in the summer by 39% and increased CO_2 influxes in the winter by 15%. In northern waters within 35°N–45°N, the summer CO_2 effluxes were reduced by an average of 14%, whereas the winter CO_2 influxes were increased by 7% (Table 3). Thus, the depressions of skin temperature caused slight increases in the CO_2 influxes but relatively larger decreases in the CO_2 effluxes. The total effect for the whole year was an increased estimate of CO_2 sink especially in the low-latitude zones.

As stated earlier, when using eq. (2) to compute net CO_2 flux, the estimate of the CO_2 exchange coefficient could differ by a factor of 1.5–2.0 depending on the formulation being used. For the same ΔfCO_2 value, the respective CO_2 fluxes estimated by using the two different formulations would also differ by the same factor. The uncertainty in the ΔT adjustment is therefore much smaller than the uncertainty in the choice of the CO_2 exchange coefficient.

There were differences in the magnitude of the net CO_2 flux between El Niño and non-El Niño periods in the northeast Pacific. Although changes in the ΔfCO_2 value could explain part of the difference, the overriding factor seem to be the changes in wind speed during an El Niño event. While the summer/autumn CO_2 effluxes before and after the 1986/1987 El Niño within 15°N–35°N averaged about 0.6 mmol $m^{-2} d^{-1}$, the average effluxes during the El Niño was reduced to 0.4 mmol $m^{-2} d^{-1}$. Likewise, the magnitude of CO_2 influxes in winter/spring during the non-El Niño periods averaged about -2.2 mmol $m^{-2} d^{-1}$, but reduced to about -1.7 mmol $m^{-2} d^{-1}$ during the El Niño. In general, the magnitude of the ΔfCO_2 values during the 1986/1987 El Niño were larger than the respective values observed before the El Niño (Wong et al., 1995). The decreases in net CO_2 fluxes might therefore be attributed to the weaker wind observed at the low-latitude region during the El Niño (Table 2).

In northern waters within 35°N–45°N, there was a decrease in the magnitude of ΔfCO_2 during the winter of 1986/1987 but the CO_2 influxes actually increased during the same period. As in the low-latitude regions, these increases in the CO_2 fluxes were the result of increased wind stress during El Niño (Table 2). Stronger winds were generally observed in this zone during the El Niño, especially in January 1987 when wind speeds were much higher than those recorded in the other January months during the study period. The condition was slightly different in the the summer season when CO_2 effluxes in 1987 were much larger than effluxes in 1985 before the El Niño. It was the result of a combination of increased ΔfCO_2 and high wind speed between summer of 1985 and summer of 1987 (Table 2).

Integrated annually, the southwest Pacific within 25°S–15°S for the period between January 1985 and February 1988 was a CO_2 sink of -0.5 mol $m^{-2} a^{-1}$ with about -0.7 mol $m^{-2} a^{-1}$ in austral winter/spring and -0.3 mol $m^{-2} a^{-1}$ in austral summer/autumn. In the northeast Pacific within 15°N–45°N, the region during the same period was also a net CO_2 sink of -0.4 mol $m^{-2} a^{-1}$ with influx of -1.1 mol $m^{-2} a^{-1}$ in the boreal winter/spring and an efflux of 0.3 mol $m^{-2} a^{-1}$ in the boreal summer/autumn (Table 3).

4. Conclusions

Assessments of the bulk-skin temperature deviation in the Pacific mixed layer suggested an

averaged ΔT of about 0.3°C. The cooler skin temperature translated into a difference of about 0.8% in the CO_2 solubilities between the bulk mixed layer and the surface skin. The skin-temperature adjustments increased the net fluxes within 25°S–15°S by 5% in austral winter and 56% in austral summer. Within 15°N–35°N, the adjustments lowered the summer effluxes by 39% but increased the winter influxes by 15%. Similarly, in northern waters within 35°N–45°N, the adjustments reduced the summer effluxes by 14% whereas the winter influxes increased by 7%. On a yearly basis, the overall effect of the ΔT adjustment was an increased CO_2 sink.

Calculations of CO_2 flux from observations collected during the cruises showed that the northeast subtropical Pacific within 15°N–35°N was a CO_2 sink during boreal winter/spring. With the skin-temperature adjustments, the net CO_2 flux to this oceanic area averaged about -1.7 mmol $m^{-2} d^{-1}$ during the 1986/1988 El Niño and about -2.2 mmol $m^{-2} d^{-1}$ during the non-El Niño periods. The average CO_2 effluxes from the same area during boreal summer/autumn were respectively about 0.4 mmol $m^{-2} d^{-1}$ and 0.6 mmol $m^{-2} d^{-1}$ during the El Niño and the non-El Niño periods. In northern waters within 35°N–45°N, the summer net CO_2 fluxes averaged about 1.4 mmol $m^{-2} d^{-1}$ while the average of winter/spring fluxes was about -5.2 mmol CO_2 $m^{-2} d^{-1}$. However, the southwest subtropical Pacific was basically a CO_2 sink year round with net CO_2 fluxes averaged about -2.0 mmol $m^{-2} d^{-1}$ in austral winter/spring and -0.7 mmol $m^{-2} d^{-1}$ in austral summer/autumn.

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