

MRI measurements of partial pressure of CO₂ in surface waters of the Pacific during 1968 to 1970: re-evaluation and comparison of data with those of the 1980s and 1990s

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ABSTRACT

During 1968 to 1972, scientists of the Meteorological Research Institute/Japan Meteorological Agency measured CO₂ in the surface seawater and overlying air in the Pacific Ocean quasi-continuously to examine CO₂ exchange between the sea and the atmosphere. From the data remaining in our laboratory from that time, we re-evaluated the partial pressure of CO₂ in surface seawater ($p\text{CO}_2^s$) by taking into account pressure broadening effects due to the use of CO₂-in-N₂ standards, the use of chemical desiccant (Mg(ClO₄)₂), calibration using background air data, seawater temperature rise between the equilibrator and sea surface, the WMO CO₂ mole fraction scale, and differences in pressure during the oceanic CO₂ measurements from those of standards and background air in the nondispersive infra-red gas analyzer cell. The overall uncertainty of $p\text{CO}_2^s$ measurements for the cruises from 1968 to 1970 was estimated to be less than 3.6 μatm , which allowed us to evaluate temporal variations in the carbonate system over a few decades, but uncertainty was higher ($> 10 \mu\text{atm}$) for the cruise from 1971 to 1972 because of serious malfunctions of the system. The re-evaluated $p\text{CO}_2^s$ data from 1968 to 1970 exhibit patterns similar to those observed at the same place and time of year (within 30 days) in 1982/83, 1988, 1995 and 1996, but compared with levels in the 1980s and 1990s the $p\text{CO}_2^s$ level was clearly lower in the wide area of the Pacific except south of the Subtropical Front (STF; 47°S) in the Australian sector. The observed $p\text{CO}_2^s$ increased by $34 \pm 5 \mu\text{atm}$ ($n = 133$) for the area 7°N to 35°N, 138°E to 147°E from February 1969 to February 1995, $29 \pm 5 \mu\text{atm}$ ($n = 247$) for the area 9°N to 35°N, 138°E to 165°E from February 1970 to February/March 1996, $26 \pm 7 \mu\text{atm}$ ($n = 224$) for the area 29°N to 51°N, 170°W from April 1970 to April 1988, and $41 \pm 9 \mu\text{atm}$ ($n = 165$) for the area 10°S to 45°S, 148°E to 166°E from January/February 1969 to January/February 1995. In the northern subtropics (7°N to 35°N, 138°E to 147°E), we estimated the long-term increase ($35 \pm 6 \mu\text{atm}$, $n = 133$) after removing seasonal variations that were obtained from the $p\text{CO}_2^s$ -sea surface temperature (SST) relationship. Observed and seasonally adjusted increases were nearly equal to those of the partial pressure of CO₂ in the air ($1.4 \mu\text{atm yr}^{-1}$) over the same time intervals. South of the STF, $p\text{CO}_2^s$ increase as found in the subtropics was not detected, mostly due to the large variability of $p\text{CO}_2^s$ (250 to 380 μatm in 1968/69) on small spatial scales. The average $p\text{CO}_2^s$ south of the STF showed large variations on time scales of months and years that affect the estimation of the growth rate of atmospheric CO₂.

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1. Introduction

By exchanging CO_2 with the atmosphere, the ocean plays an important rôle in the global carbon cycle. The net flux of CO_2 between the sea and the atmosphere is estimated as the product of the difference in partial pressure of CO_2 between the sea and the air ($\Delta p\text{CO}_2$) and the gas transfer coefficient expressed as a function of wind speed. Changes in $\Delta p\text{CO}_2$ are mostly caused by the partial pressure of CO_2 in surface seawater ($p\text{CO}_2^s$), which shows much larger variability than does that of the air ($p\text{CO}_2^a$). Thermodynamics, biological processes and ocean dynamics are factors controlling the $p\text{CO}_2^s$ (Poisson et al., 1993), and their relative importance varies with time and space. If long-term variations in $\Delta p\text{CO}_2$ occur, they lead to changes in the net CO_2 uptake by the ocean, currently estimated to be 2 Gt-C yr^{-1} (IPCC, 1996). A net uptake of 1 Gt-C yr^{-1} by the ocean requires $\Delta p\text{CO}_2$ of $-4 \mu\text{atm}$, based on an effective air-sea gas exchange coefficient of $0.07 \text{ mol m}^{-2} \text{ yr}^{-1} \mu\text{atm}^{-1}$ (Broecker et al., 1985). Therefore, the average variation in $\Delta p\text{CO}_2$ may be $-8 \mu\text{atm}$ as compared with that of the pre-industrial era.

A long-term increase in $p\text{CO}_2^s$ nearly equal to that of $p\text{CO}_2^a$ has been reported in the Southern Ocean, south of Australia (Inoue and Sugimura, 1988), in the eastern equatorial Pacific (Goyet and Peltzer, 1994), and in the western North Pacific (Inoue et al., 1995). Wong et al. (1995) reported significant annual trends of $p\text{CO}_2^s$ in the northeast and southwest subtropical Pacific. Changes in the carbonate system over a wide ocean area due to CO_2 uptake remain ambiguous. Detecting variations in $p\text{CO}_2^s$ on a time scale of years and decades is needed in order to predict future oceanic CO_2 uptake and to provide constraints on the rôle of the ocean in the global carbon cycle model.

During 1966 to 1972, the Meteorological Research Institute (MRI)/Japan Meteorological Agency (JMA) carried out a research program that measured $p\text{CO}_2^s$ and $p\text{CO}_2^a$ to examine the rôle of the ocean with respect to increase of atmospheric CO_2 . They measured $p\text{CO}_2^s$ over a wide area of the Pacific on board the *R/V Hakuho-maru* (Ocean Research Institute, University of Tokyo). From the remaining analogue recorder charts of a nondispersive infra-red gas analyzer

(NDIR analyzer, Beckman, 315A), $p\text{CO}_2$ log book, meteorological data and hydrographic station data, we re-evaluated the $p\text{CO}_2^s$ data by taking into account effects due to the use of CO_2 -in- N_2 standards (Bischof, 1975; Pearman and Garrat, 1975), the use of chemical desiccant ($\text{Mg}(\text{ClO}_4)_2$), calibration using background air data, seawater temperature rise between the equilibrator and sea surface, the WMO CO_2 mole fraction scale, and differences in pressure during the oceanic CO_2 measurements from those of standards and background air in the nondispersive infra-red gas analyzer cell, and compare spatial distributions of $p\text{CO}_2^s$ measured at the same place and time of year (within 30 days) in 1983/84 (KH83-4), 1988 (Murphy et al., 1994 RITS/ CO_2), 1994/95 (KH94-4) and 1996 (RY9601). Fig. 1 shows the cruise tracks of the *R/V Hakuho-maru*, *R/V Ryofu-maru* (Japan Meteorological Agency), and NOAA Ship Oceanographer. These cruises are the sources of the $p\text{CO}_2^s$ data collected by MRI retrieved in this work; Table 1 summarizes the cruise information.

2. Experiments

The $p\text{CO}_2$ measuring system consisted of the NDIR analyzer, two columns of $\text{Mg}(\text{ClO}_4)_2$, two diaphragm pumps, a flow meter, a series of electromagnetic valves and a showerhead-type equilibrator (Fig. 2; redrawn from Fig. 2 in Miyake et al., 1974). Air was pumped at 10 l min^{-1} from an inlet installed at the bow of the ship to avoid contamination. Aliquots of sample air (0.5 l min^{-1}) were introduced into the sample cell of the NDIR analyzer after drying. Seawater was pumped up continuously from about 4 m below the surface into the equilibrator. The fixed volume of air (ca. 2 l) circulated at the rate of 0.5 l min^{-1} in a closed circuit, consisting of the NDIR analyzer, the diaphragm pump, the equilibrator, and the column of $\text{Mg}(\text{ClO}_4)_2$ (dashed line in Fig. 2).

Before and after the change of chemical desiccant, the difference in output voltage of the NDIR analyzer correspond to 0–1 ppm, which is probably caused by the effect of water vapor in the sample gas. The output voltage of the NDIR analyzer was recorded on a recorder chart. We

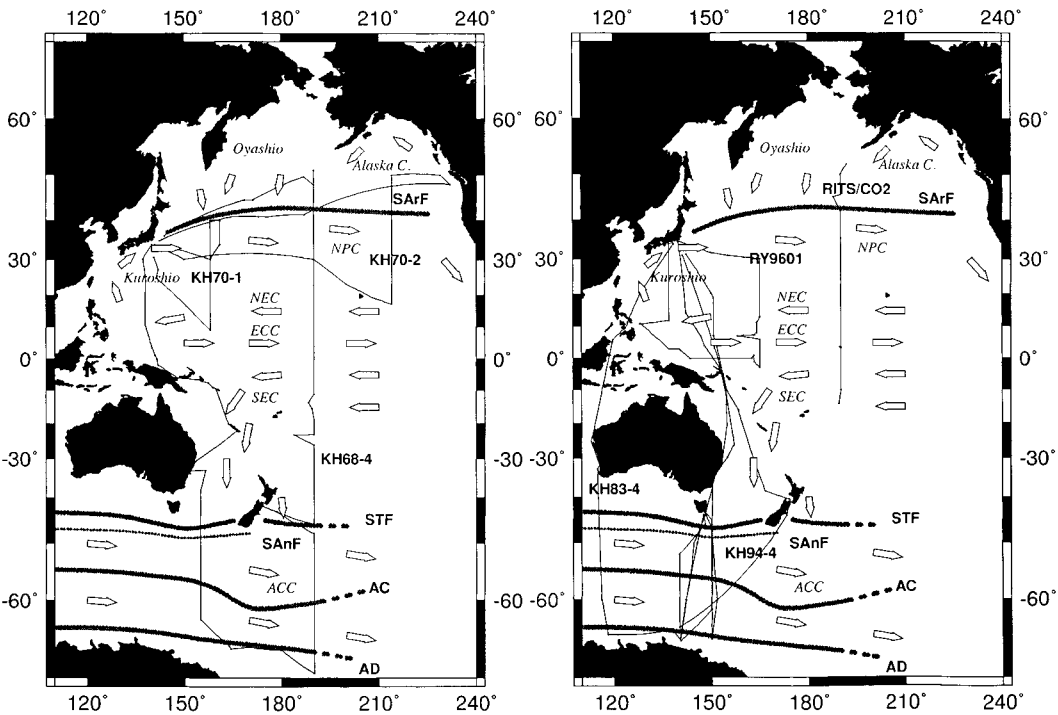


Fig. 1. Cruise tracks for the MRI $p\text{CO}_2^s$ measuring program 1968–1970 (left panel), and those of $p\text{CO}_2^s$ measurements (right panel) in 1983/84 (KH83-4), 1988 (RITS/CO₂, NOAA/PMEL), 1994/95 (KH94-4), and 1996 (RY9601). Major currents and fronts are taken from figures of Svedrup et al. (1949) and Gordon (1972). NPC is the North Pacific Current, NEC the North Equatorial Current, ECC the Equatorial Counter-Current, SEC the South Equatorial Current, and ACC the Antarctic Circumpolar Current. SA_rF is the Subarctic Front, ST_F the Subtropical Front, SA_nF the Subantarctic Front, AC the Antarctic Convergence, and AD the Antarctic Divergence. Fig. 1 was drawn by the software GMT-3 (Wessel and Smith, 1991).

Table 1. Summary of $p\text{CO}_2^s$ measurements during 1968 to 1970, and 1983/84, 1988, 1994/95, and 1996

Year	Cruise name	Departure/arrival ports	Dates	Ref.
1968/69	KH68-4	Tokyo/Tokyo	14 November–3 March	Miyake et al. (1974)
1970	KH70-1	Tokyo/Tokyo	3 February–5 March	Miyake et al. (1974)
1970	KH70-2	Tokyo/Tokyo	14 April–18 June	Miyake et al. (1974)
1983/84	KH83-4	Tokyo/Tokyo	23 November–24 February	Inoue and Sugimura (1988)
1988	RITS/CO ₂	Dutch Harbor/Am. Samoa	6 April–5 May	Murphy et al. (1994)
1994/95	KH94-4	Tokyo/Tokyo	23 November–15 February	
1996	RY9601	Tokyo/Tokyo	17 January–6 March	

digitized the analogue data by an oscillogram tracer (Ot-70 Kyoto Denshi Co., Ltd.). The resolution for analogue-to-digital conversion was better than 0.1 ppm.

2.1. Measurements of $p\text{CO}_2^s$ during 1968 to 1972
2.1.1. Measurements of $p\text{CO}_2^s$ in the KH68-4 cruise. Measurements of CO₂ concentration in the dry air equilibrated with seawater ($x\text{CO}_2^{\text{sw}}$) and

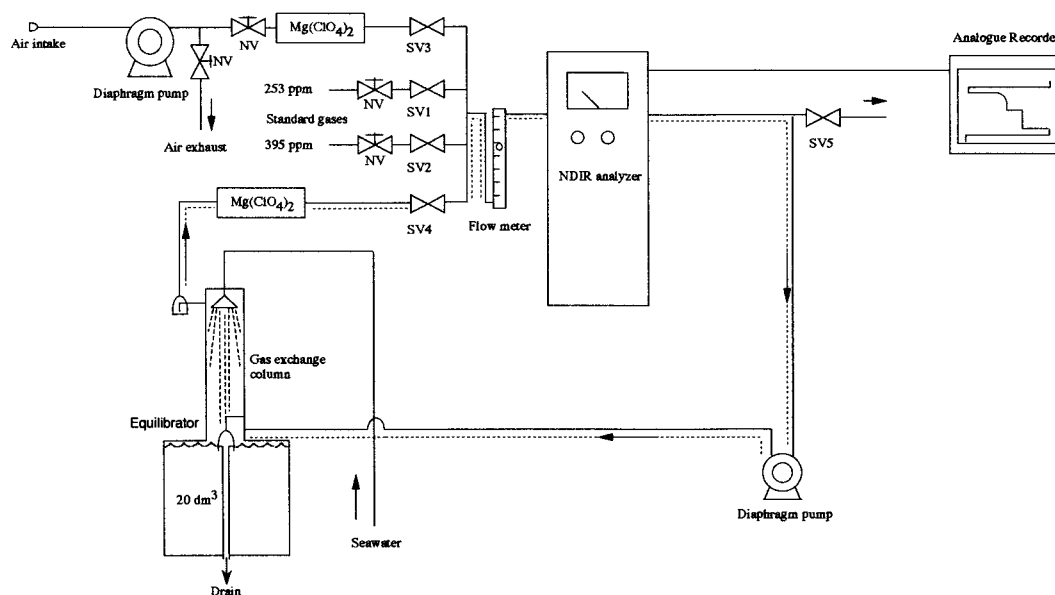


Fig. 2. A schematic diagram of the atmospheric and oceanic CO_2 measuring system used during 1968 to 1972 (redrawn from Fig. 2 in Miyake et al., 1974). Dotted line shows the air flow for oceanic CO_2 measurement. The output voltage of the NDIR analyzer was recorded on a strip chart recorder, from which the CO_2 concentrations of sample air were computed. SV = solenoid valve; NV = flow control valve.

overlying air ($x\text{CO}_2^a$) using the NDIR analyzer started in 1966 (Miyake and Sugimura, 1969). This system was constructed for measuring $x\text{CO}_2^{\text{sw}}$ in discrete samples of seawater taken on board. Miyake et al. (1974) reported its use for quasi-continuous measurements during 1968 to 1972 by operating a series of solenoid valves with an electro-mechanical device. However, for the KH68-4 cruise the record contains only local daytime data (ca. 16/day) and variable air circulation time for $p\text{CO}_2^s$ measurements. Except for the time of calibration and $x\text{CO}_2^{\text{sw}}$ measurements, air taken from the bow of the ship passed through the sample cell of the NDIR analyzer. These suggest that the operation of the solenoid valves was conducted manually.

In order to calibrate the system, two standard gases (253 ppm and 395 ppm in CO_2 -in- N_2) were introduced into the NDIR analyzer's cell every 2 or 3 days. Between two successive calibrations, we assumed a constant increase of the output voltage of the NDIR analyzer between low and high standards. From the output voltage of atmospheric CO_2 prior to oceanic CO_2 measurements, we calculated the output voltage (V) for low and high

standards by subtracting from and adding to that of the background air, respectively. The output voltages for the two standards and atmospheric CO_2 were used to calculate the $x\text{CO}_2^{\text{sw}}$,

$$x\text{CO}_2^{\text{sw}} = a + bV + cV^2, \quad (1)$$

where the coefficients (a , b , c) of the second-degree polynomial were determined by solving the equation. The difference in $x\text{CO}_2^{\text{sw}}$ raised from calibration once every few days was compared with data calibrated every hour in February 1970. The average difference for $x\text{CO}_2^{\text{sw}}$ determined at the constant difference in output voltage between the low and high standards from that of calibration every hour was -0.3 ± 0.3 ppm ($n = 60$).

2.1.2. Measurements of $p\text{CO}_2^s$ in the KH70-1 and KH70-2 cruises. The system was operated by an electro-mechanical timing device that repeated the same switching with a cycle of 1 h. For the purpose of calibration of the system, high and low CO_2 standard gases were introduced into the sample cell of the NDIR analyzer at a flow rate of 0.5 l min^{-1} successively for 5 min. Following the calibration, 25 min were allocated for the measure-

ments of $x\text{CO}_2^{\text{sw}}$ and the next 25 min for $x\text{CO}_2^{\text{a}}$ (Fig. 3). Drifts of output voltages were interpolated linearly, and the output voltage at the end of the $x\text{CO}_2^{\text{sw}}$ measurements was digitized.

In order to conserve the working standards, sometimes only low or high standard gas was introduced not the NDIR analyzer's cell (25% of the total). To calculate $x\text{CO}_2^{\text{sw}}$ by eq. (1), we

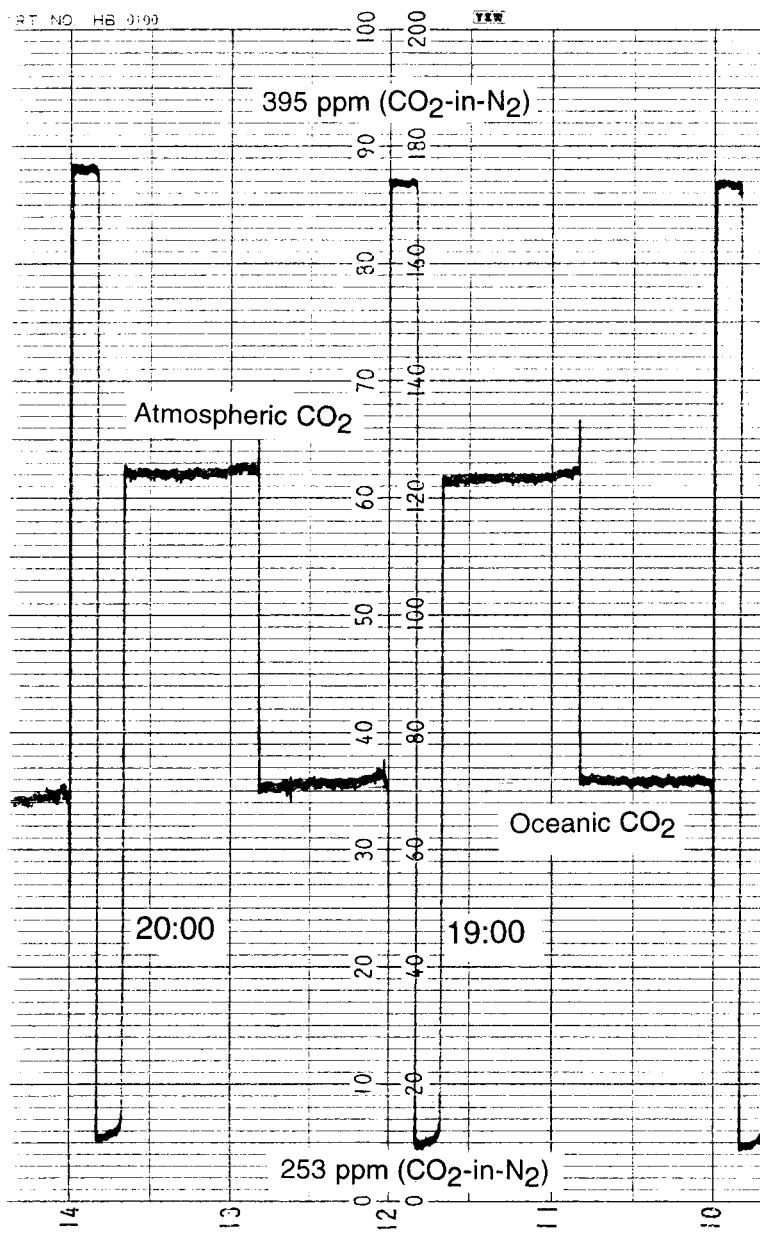


Fig. 3. Analogue recorder chart of the NDIR analyzer output voltage measured on 20 February 1970. Every hour, two standards (253 and 395 ppm CO_2 -in- N_2) were introduced into the NDIR analyzer's cell for 5 min each. Then air equilibrated with seawater or ambient air were introduced into the NDIR analyzer's cell for 25 min.

assume the following relationship:

$$\begin{aligned} V_{H(0)} - V_{A(0)} : V_{A(0)} - V_{L(0)} \\ = V_{H(t)} - V_{A(t)} : V_{A(t)} - V_{L(t)}, \end{aligned} \quad (2)$$

where $V_{H(0)}$ is the output voltage for high standard gas when $t = 0$, $V_{L(0)}$ is that for low standard gas, and $V_{A(0)}$ that for atmospheric CO_2 . If V_L or V_H was missing at time t , we estimated V_H or V_L by eq. (2). Comparison of $x\text{CO}_2^{\text{sw}}$ derived from eq. (2) was made using the data collected in February 1970. The $x\text{CO}_2^{\text{sw}}$ calculated from the output voltage from only low or high standard gas and background air deviated by 0.1 ± 0.2 ppm ($n = 60$) from that derived using both low and high standards and background air.

2.1.3. Measurements of $p\text{CO}_2^s$ in the KH71-5 cruise. Judging from the remaining analogue recorder charts and log book for $p\text{CO}_2^s$ measurements, we had two serious problems in re-evaluating the $p\text{CO}_2^s$ data: the noise level was often high (7 ppm), several times higher than that of 1968/69 and 1970; and the analogue recorder charts often exhibited a step change or a steep drift of output voltage during measurements. In this paper we do not report $p\text{CO}_2^s$ measured during 1971 to 1972.

2.2. Pressure broadening effect on the $x\text{CO}_2$ determination

CO_2 -in- N_2 standards were used in the 1968/72 cruises. Therefore, we need to determine the pressure broadening effect on the determination of $x\text{CO}_2$ by the same model of NDIR analyzer during 1968 to 1972. Inoue and Sugimura (1988) estimated this effect on the basis of standard gases (CO_2 -in- N_2 and CO_2 -in-synthesized-air) prepared by Takachiho Kagaku Co., Ltd. The manufacturer used an NDIR analyzer to determine the CO_2 concentration in N_2 ($x\text{CO}_2(\text{N}_2)$) by a series of CO_2 -in- N_2 standards prepared gravimetrically. Inoue and Sugimura (1988) compared values determined by CO_2 -in- N_2 standards ($n = 8$) with those determined by CO_2 -in-synthesized-air standards. The least-squares fit to the data yields:

$$\begin{aligned} x\text{CO}_2(\text{Sy}) = -18.54 + 1.14 \times x\text{CO}_2(\text{N}_2) \\ - 2.198 \times 10^{-4} \times (x\text{CO}_2(\text{N}_2))^2, \end{aligned} \quad (3)$$

where $x\text{CO}_2(\text{Sy})$ is the CO_2 concentration determined by the CO_2 -in-synthesized-air standards. The standard error of estimate was calculated to be ± 0.3 ppm.

2.3. The relationship between output voltage of the NDIR analyzer and CO_2 concentration

To calculate $x\text{CO}_2^{\text{sw}}$ by eq. (1), we used atmospheric CO_2 as the standard gas. Latitudinal distribution, seasonal cycle and long-term trend of atmospheric CO_2 levels over the ocean for 1968 to 1972 were estimated based on the data of Keeling et al. (1989). Latitudinal distribution of the seasonally adjusted concentration of atmospheric CO_2 ($\Delta x\text{CO}_2^{\text{lat}}$) was expressed as differences from the concentration of atmospheric CO_2 at the South Pole. Seasonal variation of atmospheric CO_2 ($x\text{CO}_2^{\text{se}}$) at the time and latitude of the cruise measurements of $p\text{CO}_2^s$ was calculated by:

$$\begin{aligned} x\text{CO}_2^{\text{se}}(y_t) = A_1 \cos(2\pi y_t + \phi_1) \\ + A_2 \cos(4\pi y_t + \phi_2), \end{aligned} \quad (4)$$

where y_t is in years, and A_1 , A_2 , ϕ_1 , and ϕ_2 are parameters reported by Keeling et al. (1989). These parameters were, however, given to show the seasonal variation of atmospheric CO_2 in 1980. To produce latitudinal distribution of atmospheric CO_2 for 1968 to 1972, we reduced the amplitude of seasonal variation of atmospheric CO_2 (Keeling et al., 1989, 1996) by assuming a linear trend between 1968 and 1980 (92.3% in 1968, Keeling et al., 1989).

The atmospheric CO_2 data were thus finally represented by:

$$x\text{CO}_2^{\text{a}} = \Delta x\text{CO}_2^{\text{lat}} + x\text{CO}_2^{\text{se}} + x\text{CO}_2^{\text{tr}}, \quad (5)$$

where $x\text{CO}_2^{\text{tr}}$ shows the long-term trend of atmospheric CO_2 at the South Pole.

2.4. Temperature rise between the equilibrator and sea surface temperature

Miyake et al. (1974) did not correct for the effect of temperature rise between the equilibrator and the sea surface on $p\text{CO}_2^s$ measurements. In our previous work (Inoue and Sugimura, 1988), we assumed a constant temperature rise ($+0.3^\circ\text{C}$) for the KH68-4 cruise. Seawater temperature in the equilibrator (T_{EQ}) and SST were recorded during 17 January to 28 February in 1969. However, in that work, we could not find these data. We assumed a linear relationship between T_{EQ} and SST, and applied it to each cruise.

$$T_{\text{EQ}} = 0.968 \times \text{SST} + 1.13, \quad (6)$$

in which the correlation coefficient r was 0.9998 ($n = 350$). In this work, we use the equation given by Gordon and Jones (1973, G&J equation) to calculate $p\text{CO}_2^s$ from the $p\text{CO}_2$ in the equilibrator.

2.5. Pressure effect on $x\text{CO}_2^{\text{sw}}$ determination

Gas circulation by the diaphragm pump leads to pressure changes in the various parts of the closed loop. Changes in pressure in the sample cell are dependent on the flow rate and the order of connections among the respective parts. During the 1968/72 cruises, the air output of diaphragm pump was connected to the inlet of equilibrator (Fig. 2). In this study, we have estimated the pressure effect by circulating air in the closed circuit of the CO_2 measuring system used during 1987 to 1993. The size of the equilibrator was almost same as that used prior to 1973, and the diameter of tubing (1/4"), and orifice of electromagnetic valves (3 mm) were same as those used between 1968 and 1972, although the 1987/93 system contained a different electric dehumidifier and more electromagnetic valves. The pressure effect on $x\text{CO}_2^{\text{sw}}$ was examined in the North Pacific on board the *R/V Natsushima* (Japan Marine Science and Technology Center) and *T/S Hukuto-maru* (Institute for Sea Training) in 1987 and 1992. Apparent change in CO_2 concentration during circulation at a flow rate of 0.51 min^{-1} against that of the flow of standards and background air was $-1.8 \pm 0.4 \text{ ppm}$ ($n = 13$).

We observed little change in the water level (less than a few cm) of the shower-head type equilibrator during measurements, which supports the small change in pressure we derived for the 1968/72 $p\text{CO}_2$ measuring system.

2.6. Data selection for atmospheric CO_2

The objective of selecting atmospheric CO_2 data was to identify $x\text{CO}_2^s$ values that are not affected by local sources and sinks. Air CO_2 variability in cycles of a few minutes to an hour is clearly caused by local contamination. We rejected data showing instability of CO_2 concentration ($> 3 \text{ ppm}$); such instability can be seen in analogue recordings of the NDIR analyzer output on a strip-chart recorder. When contamination occurred, we simply interpolated the output voltages between contiguous clean air data.

2.7. Standard gases

In a previous report, we described in detail our standard gases in use since 1987 (Inoue et al., 1995); a brief explanation follows. Since April 1987, standard gases (CO_2 in natural air) made by Nippon Sanso have been used as primary, secondary, and working standard gases. The primary standard gases were made gravimetrically following the procedures reported by Tanaka et al. (1987). We sent our cylinders to the Japan Meteorological Agency once or twice each year to compare our scale (MRI-87) with the 1985 WMO scale. The relationship between the MRI-87 scale and the 1985 WMO scale is given by:

$$x\text{CO}_2^{\text{WMO}} = 5.410 + 0.975 \times (x\text{CO}_2^{\text{MRI-87}}) + 2.530 \times 10^{-5} \times (x\text{CO}_2^{\text{MRI-87}})^2, \quad (7)$$

where $x\text{CO}_2^{\text{WMO}}$ is the CO_2 mole fraction based on the 1985 WMO scale. However, this relationship is only tentative and may change considerably in the future. The CO_2 concentrations sent to the JMA ranged from 290 to 400 ppm. In this paper we report CO_2 concentrations based on the 1985 WMO scale as calculated by eq. (7).

2.8. Estimation of $p\text{CO}_2^s$ error during the cruises from 1968 to 1970

The overall error in $p\text{CO}_2^s$ at in situ temperature (Table 2) includes the uncertainty of $x\text{CO}_2$ determination in the dry air equilibrated with seawater in the equilibrator, and the uncertainty in $p\text{CO}_2$ arising from the correction due to the difference between equilibrator temperature T_{EQ} and SST which increased with the decrease of SST (eq. (6)). Other than the G&J equation, temperature dependence of $p\text{CO}_2^s$ (or $f'\text{CO}_2^s$) have been reported (Weiss et al., 1982; Copin-Montegut, 1988, 1989; Takahashi et al., 1993; Goyet et al., 1993; Millero, 1995). Temperature rise by eq. (6) gave results that the $p\text{CO}_2^s$ calculated by their equations agrees with that of the G&J equation within the range of $\pm 0.5 \mu\text{atm}$ in the subtropics, and $\pm 2 \mu\text{atm}$ in high latitudes. Discussing the uncertainty of these equations is beyond the scope of the present work.

We estimate the uncertainty of $x\text{CO}_2^{\text{sw}}$ that originated from $x\text{CO}_2$ measurements by the NDIR analyzer (σ_n), the use of chemical dryer $\text{Mg}(\text{ClO}_4)_2$ (σ_m), drift of output voltage of the NDIR-analyzer (σ_d), pressure broadening effect (σ_{pb}), CO_2 concen-

Table 2. $1\text{-}\sigma$ uncertainties in the measurement of $p\text{CO}_2^s$ observed aboard the *R/V Hakuho-maru* during 1968 to 1970

$x\text{CO}_2^{\text{sw}}$ determination	
$x\text{CO}_2$ determination in dry air using the same standards (σ_n)	0.5 ppm (Fushimi, 1987), on land; 1 ppm, on board ^{a)}
pressure broadening effect (σ_{pb})	0.3 ppm
removal of water vapor by the chemical desiccant, $\text{Mg}(\text{ClO}_4)_2$ (σ_m)	0–1 ppm
drifts of output voltage (σ_d) between two calibrations	0.3 ppm (1968/69), constant zero/span; 0.1–0.2 ppm (1970), every 1 h
CO_2 mole fraction scale of manufacturer (σ_c)	2 ppm
atmospheric $x\text{CO}_2$ equal to that of the background air (σ_a)	<2 ppm
pressure effect on $x\text{CO}_2^{\text{sw}}$ (σ_p)	0.4 ppm
WMO 1985 scale (σ_s)	0.2 ppm
$\sigma[x\text{CO}_2]$	<3.2 ppm
$p\text{CO}_2^s$ calculation	
estimation of seawater temperature rise between equilibrator and sea surface	1.5 μatm at $p\text{CO}_2^s = 350 \mu\text{atm}$ ($\pm 0.1^\circ\text{C}$)
temperature dependence of $p\text{CO}_2^s$	<0.5 μatm in subtropics
(Gordon and Jones, 1973)	<2 μatm in high latitudes
$\sigma[p\text{CO}_2^s]^b$	<3.6 μatm

^{a)} Depending on the weather conditions.

^{b)} Uncertainty of the equation given by Gordon and Jones (1973) was not included here.

The overall uncertainty in $p\text{CO}_2^s$ ($\sigma[p\text{CO}_2^s]$) was calculated using Gaussian error propagation:
 $\sigma[p\text{CO}_2^s] = \sqrt{\sum(\sigma_i)^2}$.

tration in $\text{CO}_2\text{--N}_2$ determined by the manufacturing company (σ_c), and difference between in-situ $x\text{CO}_2^a$ and background $x\text{CO}_2$ (σ_a), pressure effect (σ_p), and CO_2 mole fraction scale (σ_s). Prior to 1987 the reproducibility of $x\text{CO}_2$ determined by the gravimetric method was usually within ± 2 ppm. Therefore, we simply use ± 2 ppm as the uncertainty of CO_2 concentration determined by the manufacturer. The atmospheric CO_2 observed aboard the ship was used as the standard by assuming the zonal mean. In the study by Inoue and Sugimura (1992), the difference between in-situ $x\text{CO}_2^a$ and background $x\text{CO}_2$ fell in the range of ± 2 ppm. Apart from local contamination that can be readily seen on analogue recorder charts, the difference in $x\text{CO}_2$ from the background value was mostly caused by the transport of air masses having different CO_2 concentrations.

2.9. The $p\text{CO}_2^s$ data for 1983/84, 1988, 1994/95 and 1996

To compare the $p\text{CO}_2^s$ data measured during 1968 to 1970, we use $p\text{CO}_2^s$ data collected in 1983/84, 1988, 1994/95 and 1996 (Table 1, Fig. 1). Measurements of $p\text{CO}_2^s$ for the cruise KH94-4

were made using the underway $p\text{CO}_2^s$ measuring system that was used for two international $p\text{CO}_2$ intercomparisons held at the Scripps Institution of Oceanography in June 1994 (Dickson, 1994) and aboard the *R/V Meteor* in June 1996 (Körtzinger et al., 1996). Details of this system have been described in Inoue (1999).

3. Results and discussion

3.1. Summary of $p\text{CO}_2^s$ measurements from 1968 to 1970

3.1.1. Results of $p\text{CO}_2^s$ measurements during the KH68-4 cruise (November 1968–February 1969). Figs. 4a–c show the latitudinal and longitudinal distribution of $p\text{CO}_2^s$, concentration of nutrients ($[\text{NO}_2^-] + [\text{NO}_3^-]$), sea surface salinity (SSS) and SST measured in the North and South Pacific during November 1968 to February 1969. The $p\text{CO}_2^s$ along 170°W , measured during 23 November 1968 to 19 January 1969, exhibited high values near the equator. The $x\text{CO}_2^{\text{sw}}$ values near the equator were larger than the CO_2 concentration of the high standards. In this case, the gain of the NDIR-analyzer was decreased by half from

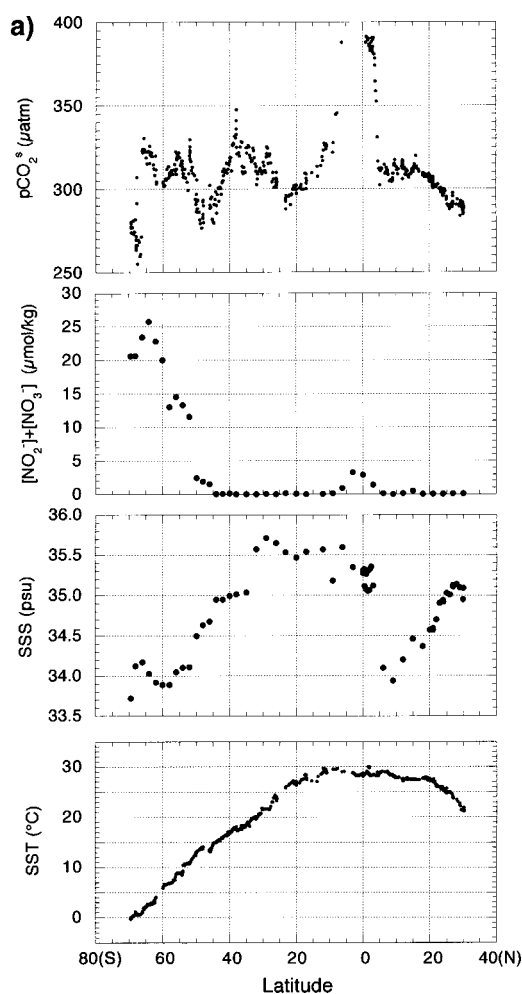


Fig. 4a. Latitudinal distribution of $p\text{CO}_2^s$, $\text{NO}_2^- + \text{NO}_3^-$, SSS, and SST along 170°W . Measurements were made from 23 November 1968 to 19 January 1969. Nutrient concentrations and SSS data were taken from hydrographic data (Preliminary Cruise Report of the Hakuho-maru, KH68-4, 1970).

that used during the cruise. However, the calibration was not carried out. In this work, we calculated the $x\text{CO}_2^{\text{sw}}$ by doubling output voltage of high standard and flagged $x\text{CO}_2^{\text{sw}}$ values during the time that the gain of the NDIR analyzer was changed. At the boundary between the North Equatorial Current and Equatorial Countercurrent (5°N) the $p\text{CO}_2^s$ changed steeply. Inoue et al. (1996) reported that changes in longitudinal distributions of $p\text{CO}_2^s$ in the central and western equa-

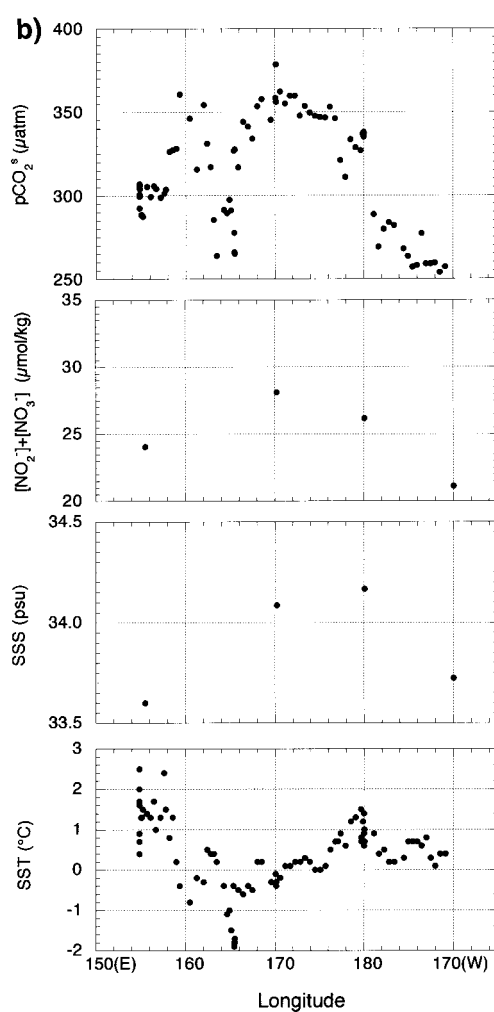


Fig. 4b. Longitudinal distribution of $p\text{CO}_2^s$, $\text{NO}_2^- + \text{NO}_3^-$, SSS, and SST measured from 19 January to 23 January 1969. Nutrient concentrations and SSS data were taken from hydrographic data (Preliminary Cruise Report of the Hakuho-maru, KH68-4, 1970). Hydrographic stations were at 69.5°S – 170°W , 66.7°S – 180° , 66.5°S – 170°E , and 63°S – 155°E .

torial Pacific were associated with the El Niño/Southern Oscillation phenomenon. In the region of the warm water pool in which SST was higher than 29°C and SSS lower than 34.5 psu, the $p\text{CO}_2^s$ was almost constant (340 to $370\ \mu\text{atm}$ in the 1990s). East of the warm water pool the $p\text{CO}_2^s$ increased along with an SST decrease and SSS increase. For the KH68-4 cruise, the hydrographic data (Oceanographic data of KH68-4,

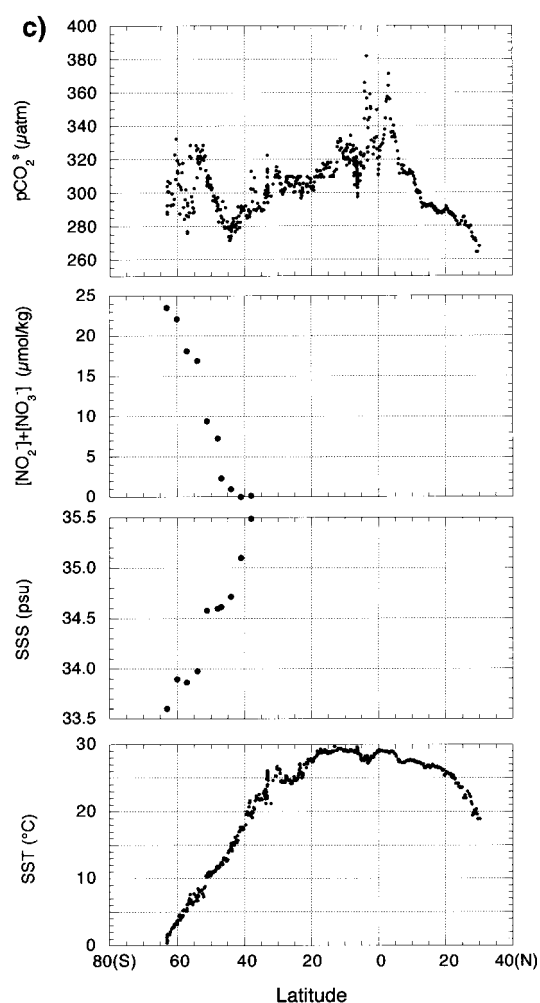


Fig. 4c. Same information as in Fig. 4a, except for the northbound leg cruise of KH68-4 (see Fig. 1), 23 January 1969 to 28 February 1969 (Preliminary Cruise Report of the Hakuho-maru, KH68-4, 1970).

1970) at the equator indicate that the SST was 28.3°C and SSS was 35.3 psu (Fig. 4a). Although the maximum value in the equatorial Pacific (>400 μatm) was not determined precisely, the $p\text{CO}_2^*$ distribution along 170°W followed the same pattern as that observed in the central and eastern equatorial Pacific, suggesting that $p\text{CO}_2^*$ was affected by the equatorial upwelling (Inoue and Sugimura, 1992; Goyet and Peltzer 1994; Feely et al., 1995; Ishii and Inoue, 1995; Wanninkhof et al., 1996).

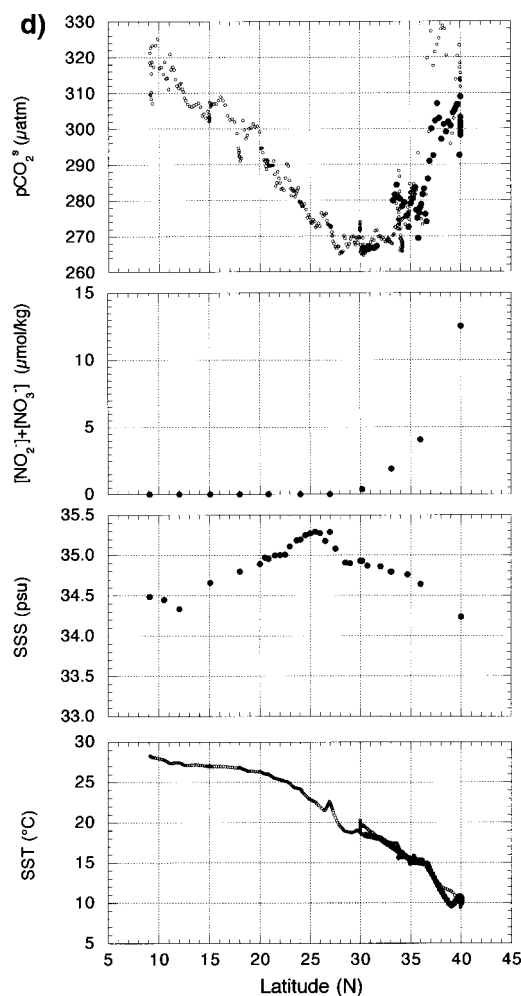


Fig. 4d. Latitudinal distribution of $p\text{CO}_2^*$, $\text{NO}_2^- + \text{NO}_3^-$, SSS, and SST along 150°E (open circles) and 161°E (solid circles). Measurements were made on 6 to 24 February 1970. Nutrient concentrations and salinity data were taken from hydrographic data (Preliminary Cruise Report of the Hakuho-maru, KH70-1, 1971).

In order to estimate the CO_2 flux between the sea and the air, the $p\text{CO}_2^*$ data in the subtropics has been interpolated by the $p\text{CO}_2^*$ -SST relationship because temperature is the main control on $p\text{CO}_2^*$ (Stephan et al., 1995). In the southern hemisphere, along 170°W surface nitrite and nitrate were depleted ($[\text{NO}_2^-] + [\text{NO}_3^-] < 1 \mu\text{mol kg}^{-1}$) from 10°S to 45°S, north of Subtropical Front. From 10°S to 23°S and from 38°S to 45°S the

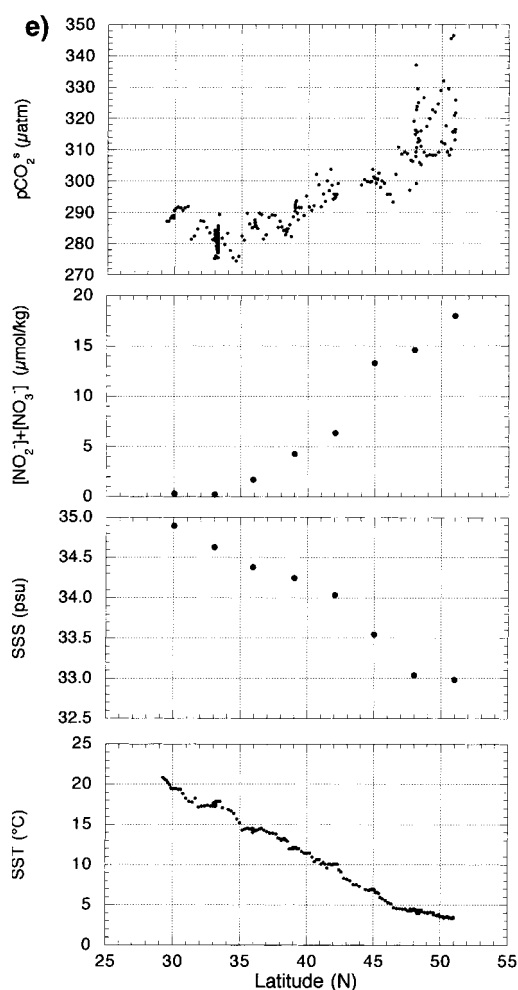


Fig. 4e. Same information as in Fig. 4d, except along 170°W, 19 to 30 April 1970 (Preliminary Cruise Report of the Hakuho-maru, KH70-2, 1971).

$p\text{CO}_2^s$ increased with SST ($3\% \text{ } ^\circ\text{C}^{-1}$). From 25°S to 38°S, however, the $p\text{CO}_2^s$ decreased with the increase of SST ($-1\% \text{ } ^\circ\text{C}^{-1}$). South of the STF, the $p\text{CO}_2^s$ changed steeply at 67°S where SST was 0.5°C. Between 45°S and 67°S, the $p\text{CO}_2^s$ ranged from 275 to 330 μatm with an average of $308 \pm 12 \mu\text{atm}$ ($n = 115$). South of 67°S, the $p\text{CO}_2^s$ from 255 to 310 μatm with the average of $274 \pm 10 \mu\text{atm}$ ($n = 28$), acted as a sink for atmospheric CO_2 ($319 \pm 1 \mu\text{atm}$, $n = 144$). No clear $p\text{CO}_2^s$ -SST relationship was found for areas south of STF. The present result indicates that repeated measurement of $p\text{CO}_2^s$ over a wide area is required

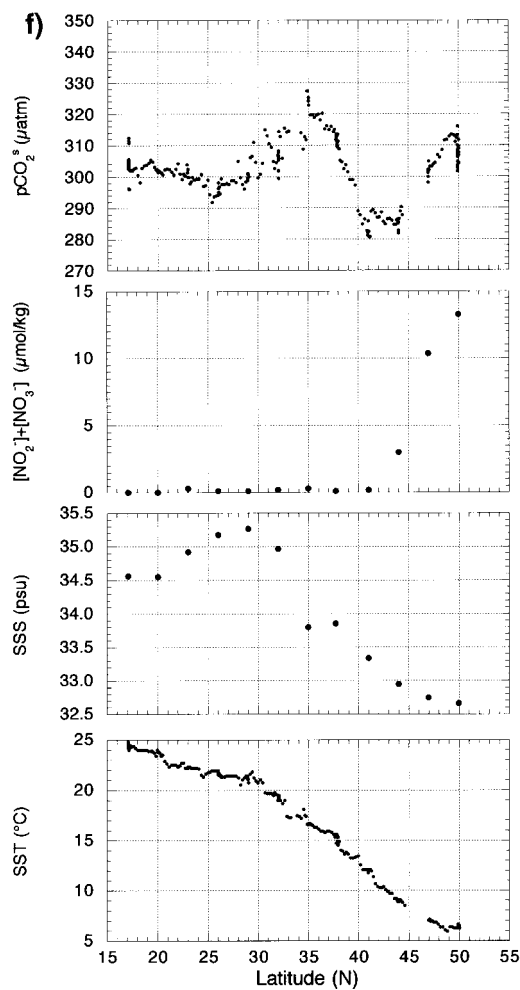


Fig. 4f. Same information as in Fig. 4d, except along 146°W, 11–23 May 1970 (Preliminary Cruise Report of the Hakuho-maru, KH70-2, 1971).

to estimate CO_2 flux between the sea and the air more accurately.

Between 155°E and 170°W, the $p\text{CO}_2^s$ showed significant meso-scale variability and ranged from 250 to 380 μatm . East of 165°E, $p\text{CO}_2^s$ tended to decrease with increasing SST (Fig. 4b). The concentration of nitrite plus nitrate of $21 \mu\text{mol kg}^{-1}$ at 69.5°S, 170°W was relatively low compared with values of $28 \mu\text{mol kg}^{-1}$ at 66.5°S, 170°E and $26 \mu\text{mol kg}^{-1}$ at 66.7°S, 180°. At 69.5°S, 170°W SSS was as low as 33.7 psu. Therefore, the lower $p\text{CO}_2^s$ south of 67°S along 170°W could be attributed to the addition of freshwater and biological

carbon uptake. Robertson and Watson (1995) have reported poor or no correlation between $p\text{CO}_2^s$ and either chlorophyll or temperature, except in areas where high chlorophyll or the southern polar front was encountered.

The $p\text{CO}_2^s$ during the northbound cruise conducted in January and February 1969 exhibited minimum values at 45°S, and increased towards the north except in the area close to 5°S. The $p\text{CO}_2^s$ was highly variable between 5°S and 5°N where the survey vessel moved close to land (Fig. 1). For the area 5°N–30°N, $p\text{CO}_2^s$ decreased with decreasing SST and $\Delta p\text{CO}_2$ was as low as $-60 \mu\text{atm}$ at 30°N, which was nearly equal to that of 1980s and 1990s (Inoue et al., 1995). North of 30°N, $p\text{CO}_2^s$ increased rather steeply with decreasing SST.

3.1.2. Measurements of $p\text{CO}_2^s$ in the western North Pacific in February 1970. The latitudinal distribution of $p\text{CO}_2^s$ along 158°E (Fig. 4d) showed a broad minimum at the area 27°N–34°N, which was the same pattern as is shown in Fig. 4c. This $p\text{CO}_2^s$ minimum occurred in an area where SST ranged from 18 to 20°C. It has been reported that subtropical mode water (19°C mode water), vertically homogeneous water found between the seasonal thermocline and the deeper main thermocline, was produced in this area (Suga and Hanawa, 1990; Bingham, 1992).

From 30°N to 40°N, measurements of $p\text{CO}_2^s$ were repeated for 6–16 February 1970. From 30°N to 35°N, the distributions of $p\text{CO}_2^s$ showed the similar pattern during this period. North of 35°N, however, distributions of $p\text{CO}_2^s$ and SST varied considerably within a few days (Fig. 4d). From 36.5°N to 38.5°N, the $p\text{CO}_2^s$ was higher than 310 μatm on 12 February, while decreased to the level of 275–310 μatm on 14 February, which is probably caused by different water masses in the area of Kuroshio front (Kawai 1972; Roden et al., 1982).

3.1.3. Measurements of $p\text{CO}_2^s$ in the North Pacific during April to June 1970. The latitudinal distribution of $p\text{CO}_2^s$ along 170°W and along 146°W showed different patterns (Figs. 4e and 4f). North of 35°N, $p\text{CO}_2^s$ along 170°W increased poleward, but was fairly constant between 40°N and 45°N. Along 146°W, $p\text{CO}_2^s$ reached a broad minimum between 40°N and 45°N. The Subarctic Front (Svedrup et al.,

1949; Roden et al., 1982) existed in this region (42°N–43°N, as indicated from the results in Figs. 3 and 11 of Preliminary Report KH70-2, 1971). The $p\text{CO}_2^s$ along 170°W increased with decreasing SST and SSS; SSS decreased to as low as 33 psu at 50°N. However, $p\text{CO}_2^s$ along 146°W showed no correlation with either SST or SSS. For both transects, the concentration of nitrate and nitrite increased poleward. In August and September, $p\text{CO}_2^s$ for the area between 46°N and 50°N exhibited a significant interannual variability, especially in the eastern North Pacific (Murphy et al., 1998). The $\Delta p\text{CO}_2$ in August 1985 decreased by 40 μatm from 162°W (20 μatm) to 155°W ($-20 \mu\text{atm}$), while in August 1987, $p\text{CO}_2^s$ increased by 30 to 40 μatm from 162°W (0 μatm) to 150°W (40 μatm). Also, Takahashi et al. (1993) reported significant seasonal variations in $p\text{CO}_2^s$ of which phase and amplitude indicate heterogeneity (Fig. 9 in Takahashi et al., 1993). Therefore, the latitudinal distribution of $p\text{CO}_2^s$ north of the Kuroshio Extension could change significantly and interannually. The $p\text{CO}_2^s$ for the region 125°W–140°E and 48°N–40°N in June 1970 (Fig. 5) exhibited a trend similar to that of August 1987.

3.2. Interannual trends in $p\text{CO}_2^s$

We used the re-evaluated $p\text{CO}_2^s$ data in this work to examine temporal variations in $p\text{CO}_2^s$

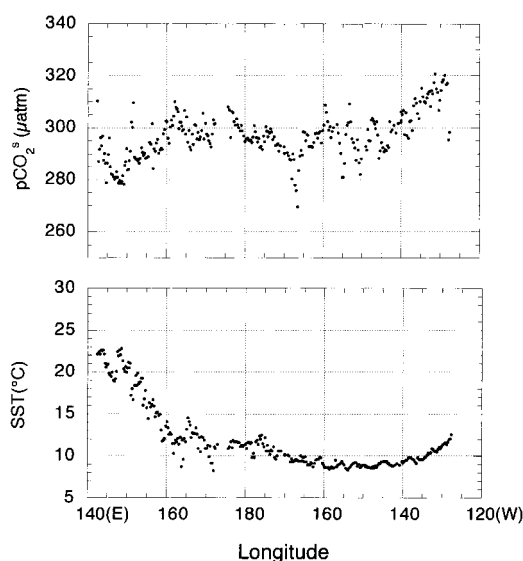


Fig. 5. Longitudinal distribution of $p\text{CO}_2^s$ and SST for the westbound cruise on 3 to 16 June 1970 (see Fig. 1).

over a few decades. The $p\text{CO}_2^s$ data in 1983/84, 1988, 1994/95 and 1996 (Table 1) that were measured almost at the same place and in the same season (within 30 days) were selected.

3.2.1. Comparison of $p\text{CO}_2^s$ data of KH68-4 with those of KH83-4 and KH94-4. Fig. 6 indicates the latitudinal distribution of $p\text{CO}_2^s$ measured during January to February 1969, January to February 1984, and January to February 1995. The area between 135°E and 155°E was selected to examine the temporal variations in $p\text{CO}_2^s$ (Fig. 1). A clear $p\text{CO}_2^s$ increase was found in the subtropics for both hemispheres (Table 3). The apparent increase of the $p\text{CO}_2^s$ between 1969 and 1995 was $41 \pm 9 \mu\text{atm}$ ($n = 165$) in the southern subtropics, and $34 \pm 5 \mu\text{atm}$ ($n = 133$) in the northern subtropics. During the same period the $p\text{CO}_2^s$ increased by $35 \mu\text{atm}$. As reported in previous studies (Goyet and Peltzer, 1994), these data include short-term variations at small spatial scales, partly due to the difference in sampling time and differences in ocean dynamics. Goyet and Peltzer (1994) used a digital filtering technique to remove short-term variations from observed $p\text{CO}_2^s$. In this work, we also fitted observed $p\text{CO}_2^s$ data to the smoothing function (KaleidaGraph Reference Guide, 1995) to see spatial distribution on basin wide scale.

In the northern subtropics, we estimated long-term trends by subtracting seasonal variations

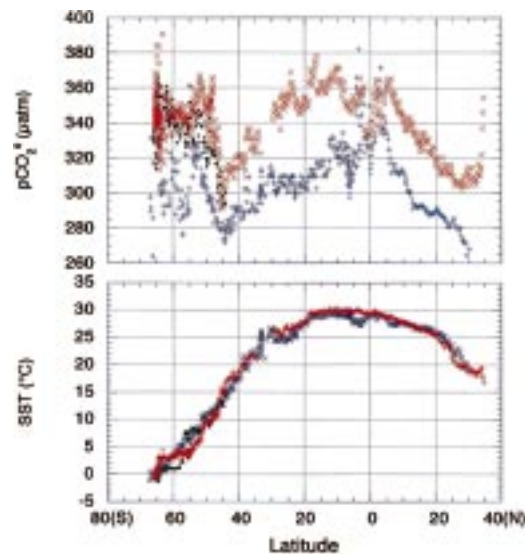


Fig. 6. Latitudinal distribution of $p\text{CO}_2^s$ and SST between 135°E and 155°E in January/February 1969, January/February 1984, and January/February 1995 (see Fig. 1). $\times$ (blue): January/February 1969; solid circles (green): January/February 1984; + (red): January/February 1995.

calculated from the $p\text{CO}_2^s$ -SST relationship. Weiss et al. (1982) reported that $p\text{CO}_2^s$ correlates well with SST in the subtropics. In the western North Pacific, the amplitude of the seasonal variation in

Table 3. The increase of $p\text{CO}_2^s$ and $p\text{CO}_2^a$ (Δ)

Period	Latitude	Longitude	Δ (μatm)	$1-\sigma$ (μatm)	No.	
February 1969–February 1995	7°N–35°N	138°E–147°E	34.3	4.9	133	OBS
			35.1	5.5	133	SA
			37.3	5.4	133	NO
			36.2	1.3	133	AIR
January/February 1969–January/February 1995	10°S–45°S	148°E–166°E	40.8	8.5	165	OBS
			27.5	9.5	165	NO
			34.4	0.5	165	AIR
February 1970–February/March 1996	9°N–35°N	158°E–165°E	29.0	4.6	247	OBS
			29.0	8.3	247	NO
			36.6 ^{a)}	0.7	135	AIR
April 1970–April 1988	29°N–51°N	170°W	25.5	7.2	224	OBS
			48.2	16.0	224	NO
			24.4	2.8	224	AIR

^{a)} Data south of 30°N were used.

Seasonal variations in the northern subtropics (8°N – 35°N) were estimated by the $p\text{CO}_2^s$ -SST relationship (Inoue et al., 1995). OBS means the observed data, SA the seasonally adjusted, NO the normalized $p\text{CO}_2^s$ by thermodynamic temperature dependence, AIR the $p\text{CO}_2$ in the ambient air.

$p\text{CO}_2^s$ was about 2/3 of values expected from the thermodynamic temperature effect. Inoue et al. (1995) reported the apparent relationship between $p\text{CO}_2^s$ and SST for the area 132°E – 142°E in the western North Pacific; except in the boundary area between two currents, the correlation coefficients were usually higher than 0.85. Applying the $p\text{CO}_2^s$ -SST relationship to the February 1995 data, we calculated the $p\text{CO}_2^s$ in 1995 when the 1995 SST was equal to that of 1969 (Fig. 7). For comparison, the 1995 $p\text{CO}_2^s$, assuming that the thermodynamic temperature effect took place, is also plotted in the same figure. In the subtropics observed and seasonally adjusted (or thermodynamically calculated) increases were nearly equal to those of the partial pressure of CO_2 in the air ($1.4 \mu\text{atm yr}^{-1}$) over the same time intervals.

Wong et al. (1995) reported that $p\text{CO}_2^s$ during summer has shown an extraordinary long-term increase. Although our summer $p\text{CO}_2^s$ data in the southern subtropics appear to show large increases compared with those of the air, the larger part of

the increase was caused by change in $p\text{CO}_2^s$ due to the difference in SST between the two periods (Fig. 8, Table 3).

In the southwestern equatorial Pacific, the survey vessel passed through a different strait in 1969 than in 1995 (Fig. 1). Therefore, we do not compare the $p\text{CO}_2^s$ directly between these two cruises.

It was not clear whether there was an increase in $p\text{CO}_2^s$ in the area south of 45°S because there was large variability on small spatial scales. South of 40°S , the ship crossed the major fronts, namely the STF, the Subantarctic Front (SAF), and the Antarctic Polar Front (APF). Judging from the vertical profiles of temperature and salinity, the STF was at around 47°S during the cruises. On the basis of $p\text{CO}_2^s$ data between 1983/84 and 1969, Inoue and Sugimura (1988) reported that the increase of $p\text{CO}_2^s$ south of the STF over this period ($32 \mu\text{atm}$) was larger than that in the subtropics. The difference in $p\text{CO}_2^s$ between January/February 1995 and January/February 1984, however, was

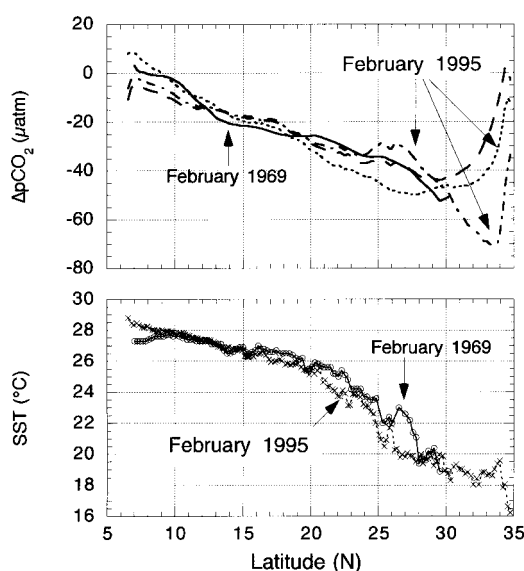


Fig. 7. Latitudinal distribution of $\Delta p\text{CO}_2$ and SST for the area 7°N – 35°N , 135°E – 150°E in February 1969 and 1995. Upper panel: solid line, $\Delta p\text{CO}_2$ in February 1969; dotted line, $\Delta p\text{CO}_2$ in February 1995; dashed line, $\Delta p\text{CO}_2$ in February 1995, seasonally adjusted by the $p\text{CO}_2^s$ -SST relationship; dashed-dotted line, $\Delta p\text{CO}_2$ in February 1995, normalized to the SST in February 1969. Lower panel: open circles, February 1969; x, February 1995.

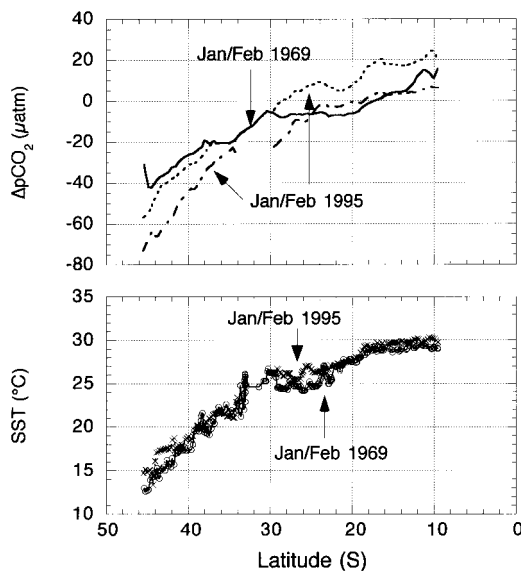


Fig. 8. Latitudinal distribution of smoothed $\Delta p\text{CO}_2$ and observed SST for the area 7°S – 45°S , 135°E – 155°E in January/February 1969 and 1995. Upper panel: solid line, $\Delta p\text{CO}_2$ in January/February 1969; dotted line, $\Delta p\text{CO}_2$ in January/February 1995; dashed line, $\Delta p\text{CO}_2$ in January/February 1995, normalized to the SST in January/February 1969. Lower panel: open circles, January/February 1969; x, January/February 1995.

only $7 \mu\text{atm}$ (Fig. 9). In order to elucidate the long-term trend we need to remove short-term and small-spatial-scale variations from the observed data. Seasonal variations south of the STF have not been characterized well. Along 150°E , we observed $p\text{CO}_2^s$ three times from 42°S to 65°S between December 1983 and January 1984. Variations in $p\text{CO}_2^s$ south of the STF were small and not correlated with SST (Inoue and Sugimura, 1988). Fig. 9 indicates that south of the STF long-term trend in $p\text{CO}_2^s$ as found in the subtropics could not be detected because of significant variations on time scales of months to years. Variations in $p\text{CO}_2^s$ lead to changes in oceanic CO_2 uptake in the Southern Ocean, where the gas transfer coefficient is high due to high wind speed. On the basis of atmospheric CO_2 data, Conway et al. (1994) reported that the Southern Ocean acted as a strong sink between 1989 and 1992 and a weak sink from 1981 to 1987. Francey et al. (1995) and Keeling et al. (1995) have also reported interannual variations in oceanic CO_2 uptake based on carbon isotope analysis of atmospheric CO_2 . Our results indicate that variations in $\Delta p\text{CO}_2$ in the Southern Ocean are larger than those in the subtropics and lead to appreciable changes in CO_2 flux between the sea and the atmosphere.

3.2.2. Comparison of $p\text{CO}_2^s$ data of KH70-1 with those of RY9601. Fig. 10 compares the latitudinal distribution of $p\text{CO}_2^s$ between 158°E and 161°E in February 1970 with that along 165°E in

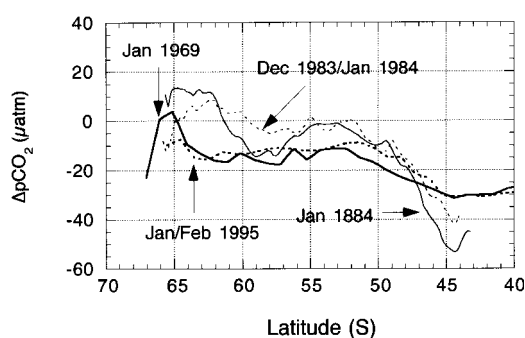


Fig. 9. Latitudinal distribution of smoothed data of $\Delta p\text{CO}_2$ south of 40°S in January 1969 (solid line), December 1983/January 1984 (thin dotted line), January 1984 (thin solid line), and January/February 1995 (dotted line).

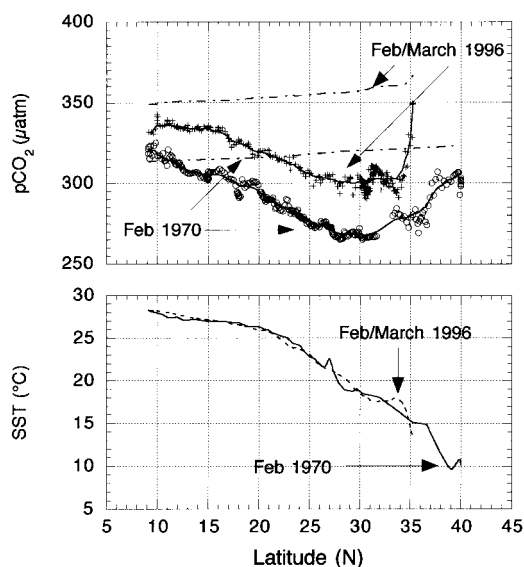


Fig. 10. Latitudinal distribution of $p\text{CO}_2^s$ and $p\text{CO}_2^a$ between 141°E and 165°E in February 1970 and February/March 1996. North of 35°N relatively large short-term variation in $p\text{CO}_2^s$ occurred. In this figure $p\text{CO}_2^s$ data observed in 14–24 February 1970 were plotted (see text). Upper panel: open circles, $p\text{CO}_2^s$ in February 1970; +, $p\text{CO}_2^s$ in February/March 1996. Solid line represents the smoothed $p\text{CO}_2^s$ and sash-dotted line $p\text{CO}_2^a$. Lower panel: solid line, smoothed SST in February 1970; dashed line, smoothed SST in February/March 1996.

February/March 1996. Both data sets showed fairly constant longitudinal distribution of $p\text{CO}_2^s$. The $p\text{CO}_2^s$ between 10°N and 35°N showed a clear increase ($29 \pm 5 \mu\text{atm}$, $n = 247$). The $p\text{CO}_2^s$ increased with SST south of 30°N , and decreased with SST between 30°N and 40°N (Fig. 10). The increase of $p\text{CO}_2^s$ between 1970 and 1996 seems to be smaller than that of the $p\text{CO}_2^a$ ($37 \mu\text{atm}$). Between 1969 and 1995, the same interval between 1970 and 1996, the $p\text{CO}_2^a$ increased by $34 \mu\text{atm}$. A high atmospheric CO_2 level observed in 1996.

3.2.3. Comparison of $p\text{CO}_2^s$ data during the KH70-1 cruise. We compared our $p\text{CO}_2^s$ data along 170°W for the cruise conducted from April to June 1970 with measurements by NOAA/PMEL in 1988 (Murphy et al., 1994). Fig. 11 showed that the $p\text{CO}_2^s$ values in 1988 were clearly higher than those in 1970. The $p\text{CO}_2^s$ and SST distributions showed similar patterns for both

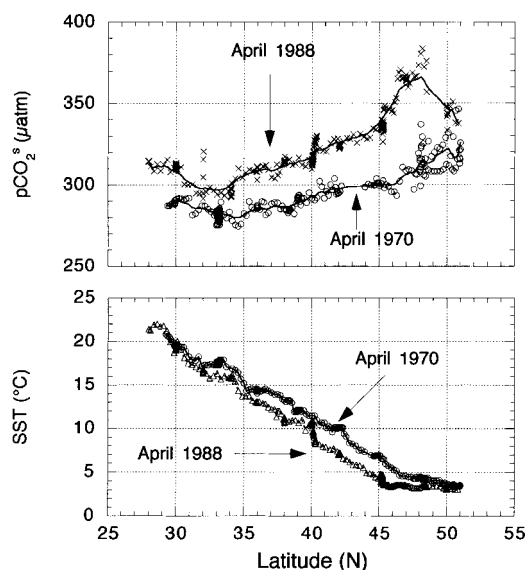


Fig. 11. Latitudinal distribution of $p\text{CO}_2^s$ and SST along 170°W in April 1970 and April 1988 (Murphy et al., 1994; RITS/ CO_2 , NOAA/PMEL). Upper panel: open circles, $p\text{CO}_2^s$ in April 1970; $\times$, $p\text{CO}_2^s$ in April 1988. Solid line represents the smoothed $p\text{CO}_2^s$. Lower panel: open circles, SST in April 1970; open triangles, SST in April 1988.

cruises, but seem to be shifted latitudinally. We plotted observed $p\text{CO}_2^s$ against SST (Fig. 12); $p\text{CO}_2^s$ showed a minimum at $16\text{--}17^\circ\text{C}$. The temperature dependence of $p\text{CO}_2^s$ reveals the same pattern as found in the western North Pacific (minimum at 19°C). The increase in $p\text{CO}_2^s$ over

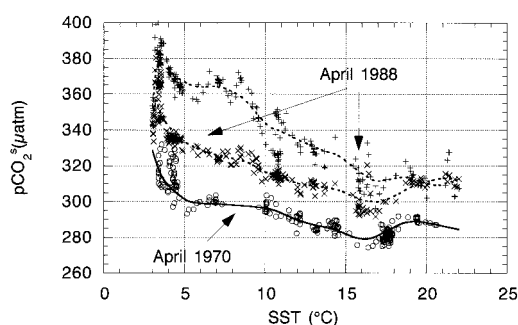


Fig. 12. Temperature dependence of observed and smoothed $p\text{CO}_2^s$ data along 170°W in April 1970 and 1988. Open circles: $p\text{CO}_2^s$ in April 1970; $\times$, $p\text{CO}_2^s$ in April 1988, $+$, $p\text{CO}_2^s$ in 1988 normalized to the SST in April 1970.

this period ($25 \pm 7 \mu\text{atm}$, $n = 224$) was nearly equal to that of the air ($24 \mu\text{atm}$). Murphy et al. (1998) reported significant interannual variations in $p\text{CO}_2^s$ in the eastern North Pacific in August and September. Generally, the $p\text{CO}_2^s$ shows large variability on small spatial scales during summer and small variability during winter (Poisson et al., 1993; Inoue et al., 1995). The interannual variations in $p\text{CO}_2^s$ during early summer may be small in comparison with those in August and September. In order to confirm the present results, repeated measurements of $p\text{CO}_2^s$ are needed.

3.2.4. The increase of $p\text{CO}_2^s$ in the subtropical, subantarctic, and subarctic regions. In the broad western Pacific ($10^\circ\text{S}\text{--}45^\circ\text{S}$, $7^\circ\text{N}\text{--}51^\circ\text{N}$), $p\text{CO}_2^s$ increased at a rate nearly equal to that of the air while keeping the same pattern. It is well-known that the CO_2 flux between the sea and the air varies over time and space (see for example, Tans et al., 1991). As reported earlier, thermodynamics, biological activity and ocean dynamics (Poisson et al., 1993) are factors controlling $p\text{CO}_2^s$. To discuss the long-term trend of $p\text{CO}_2^s$, we may need to take into account processes that have not been previously discussed to explain the short-term variations. Deposition of acid substances into the western North Pacific, which are expected to increase in fossil fuel and biomass burning and other acidic emissions, is one example. Acid rain contains the SO_4^{2-} ion that is unrelated to biological activity. Using the equations given in DOE (1994), we can calculate expected changes in $p\text{CO}_2^s$ due to this "natural titration", if the pH of the rain, and the amount of precipitation/evaporation and water mixing are known. For example, at Minamitorishima (24°N , 154°E), the wet deposition of SO_4^{2-} acted as a strong acid was $7 \text{ mmol m}^{-2} \text{ yr}^{-1}$ in 1996 (JMA, 1998). At the conditions of rapid water mixing in the surface mixed layer (50 m), $p\text{CO}_2^s$ of $300 \mu\text{atm}$, the dissolved inorganic carbon of $1935 \mu\text{mol kg}^{-1}$, SST of 19°C , and SSS of 34 psu and equal amount of annual precipitation and evaporation, the annual change in $p\text{CO}_2^s$ due to acid rain was calculated to be $0.2 \mu\text{atm yr}^{-1}$. This is large enough when we discuss the long-term trend of $p\text{CO}_2^s$. The $p\text{CO}_2^s$ is sensitive to the pH of seawater; addition of acid substances and dilution by precipitation are competitive processes that affect $p\text{CO}_2^s$. The effect of acid rain on the carbonate system could

be significant when we discuss long-term trends in $p\text{CO}_2^s$. At present we cannot detect any long-term trend in pH, probably because of relatively short time after the availability of precise pH measurements and a compensation effect between biological activity (new production) and addition of acid materials (CO_2 , SO_4^{2-} and others). Following the present increases in acid material released as a result of increase in burning of fossil fuels and biomass and in other acidic emissions, the spatial distribution of $\Delta p\text{CO}_2$ may change over the next few decades.

The present work provides $p\text{CO}_2^s$ data that will be used to examine temporal variations of the carbonate system in surface waters affected by physical, chemical and biological processes and to provide constraints in model simulation of the carbon cycle in the ocean. The $p\text{CO}_2^s$ data newly evaluated will be made available from WMO WDCGG (Tokyo, Japan) and CDIAC (Oak Ridge, USA) in the near future.

4. Conclusions

We re-evaluated $p\text{CO}_2^s$ data collected over a wide area of the Pacific from 1968 to 1972 by taking into account the pressure broadening effect due to the use of CO_2 -in- N_2 standards (Bischof, 1975; Pearman and Garrat, 1975), the use of chemical desiccant ($\text{Mg}(\text{ClO}_4)_2$), calibration using the atmospheric CO_2 data reported by Keeling et al. (1989), WMO CO_2 mole fraction scale, temperature rise between the equilibrators and the sea surface, and pressure differences in the sample cell during oceanic CO_2 measurements from those of background air and standards. The overall uncertainty was typically less than $3.6 \mu\text{atm}$ for the cruises in 1968/69 and 1970, but was higher ($> 10 \mu\text{atm}$) for the cruise in 1971/72 (which was rejected). The former was precise enough to examine the long-term trend of $p\text{CO}_2^s$.

We compared $p\text{CO}_2^s$ levels in 1968/70 with those at the same place and season (within 30 days) in 1983/84 (KH68-4), 1988 (Murphy et al., 1994 RITS/ CO_2), 1994/95 (KH94-4), and 1996 (RY9601). The observed $p\text{CO}_2^s$ increased by $34 \pm 5 \mu\text{atm}$ ($n = 133$) for the area 7°N – 35°N , 138°E – 147°E from February 1969 to February 1995; $29 \pm 5 \mu\text{atm}$ ($n = 247$) for the area 9°N – 35°N , 138°E – 165°E from February 1970 to February/March 1996;

$26 \pm 7 \mu\text{atm}$ ($n = 224$) for the area 29°N – 51°N , 170°W from April 1970 to April 1988; and $41 \pm 9 \mu\text{atm}$ ($n = 165$) for the area 10°S – 45°S , 148°E – 166°E from January/February 1969 to January/February 1995. Because direct comparison of $p\text{CO}_2^s$ data includes the seasonal variations, we estimated the long-term increase of $p\text{CO}_2^s$ ($35 \pm 6 \mu\text{atm}$, $n = 133$) by removing the seasonal variations in the northern subtropics (7°N – 35°N , 138°E – 147°E) where good $p\text{CO}_2^s$ -SST relationships have been reported (Inoue et al., 1995). If thermodynamic $p\text{CO}_2^s$ -SST relationships applied, the increase of $p\text{CO}_2^s$ in the subtropics was also nearly equal to that of observed one, but was considerably different at high latitudes. The increase in the subtropics were nearly equal to $p\text{CO}_2^s$ ($1.4 \mu\text{atm yr}^{-1}$) for the respective time intervals, which means that the oceanic CO_2 uptake in the subtropics has remained the same over the past few decades.

South of STF (47°S), we did not detect the increase of $p\text{CO}_2^s$ that was nearly equal to that of $p\text{CO}_2^s$: $305 \pm 16 \mu\text{atm}$ ($n = 125$) in 1968/69, $338 \pm 12 \mu\text{atm}$ ($n = 159$) in 1984, and $345 \pm 10 \mu\text{atm}$ ($n = 500$) in 1995. Data on $p\text{CO}_2^s$ measured in 1968/69, 1983/84 and 1994/95 suggest large interannual-decadal $p\text{CO}_2^s$ variations south of the STF. On the basis of carbon isotope measurements, interannual variations of oceanic carbon uptake have been reported (Francey et al., 1995; Keeling et al., 1995). The equatorial Pacific (Feely et al., 1987, 1995; Inoue and Sugimura, 1992; Ishii and Inoue, 1995) and Southern Ocean (Robertson and Watson, 1995) are at least partly responsible for the interannual change supported by our work here on.

Monitoring temporal and spatial variations of $p\text{CO}_2^s$ and other parameters describing the carbonate system is an essential requirement to understand the global carbon cycle and possible linkage of other environmental issues such as long range transport of the aerosols and acid rain in the ocean.

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