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pCO_2 and $\delta^{13}C$ in the air and surface sea water in the western North Pacific

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ABSTRACT

In order to ascertain yearly variability, the pCO_2 in the air and surface sea water was measured during the winter season in and over the western North Pacific from 1981 to 1985, and $\delta^{13}C$ measurements were taken from 1982. The seasonality was also studied in the area off Japan's coast. The distribution of pCO_2 in the surface sea water was found to vary with geographical location; it is low in the mid-latitudes and high in the equatorial region. During the El Niño Event in 1982/1983, the horizontal distribution of pCO_2 was greatly disturbed, with a relatively low temperature and a high pCO_2 level in the equatorial region in the western North Pacific.

Surface sea water in the temperate zone shows a seasonal variation in pCO_2, which is low in winter and high in summer.

It was found that pCO_2 in the air over the ocean decreases with distance from the Japanese islands, and south of 15°N it is nearly constant. Between 1982 and 1985, the $\delta^{13}C$ of CO_2 in the air south of 15°N decreased at 0.022 ± 0.006‰ yr^{-1} and the pCO_2 increased at 1.11 ± 0.04 ppm yr^{-1}. The secular variation of pCO_2 and $\delta^{13}C$ in the surface sea water with the CO_2 increase in the air, was not ascertainable from observations from 1981 to 1985.

1. Introduction

Man has been disturbing the global carbon budget mainly by releasing large quantities of CO_2 from fossil fuel combustion into the atmosphere. The impact of this activity is seen without a doubt in a steadily rising concentration of atmospheric CO_2. The retention of CO_2 in the atmosphere is estimated to be 56.7% of the total release, based on an examination of Mauna Loa and South Pole data (Keeling, 1983). At present, no comparable data exists to assess the disturbance of the carbon budget on the land or in the ocean. It is generally accepted that the ocean acts as one of the principal controllers of the rising concentration of the atmospheric CO_2 of recent years, along with land biomass. However, because of difficulties in understanding the CO_2 exchange process, estimations based only on the measurement of pCO_2 in the atmosphere into the amount of carbon transfer to and from the ocean and land biomass remain ambiguous in their results.

Measurement of the concentration (pCO_2) as well as the carbon isotope ratio ($\delta^{13}C$) of CO_2 in the air and in the surface sea water is one of the possible approaches to clarifying the changing global carbon budget, because the isotopic compositions of the global carbon reservoirs (atmosphere, ocean and land biomass) differ from each other. Since 1958, the determination of pCO_2 in the air and in surface sea water has been attempted by many laboratories (Takahashi, 1961; Keeling, 1968; Akiyama, 1968; Gordon et al., 1973; Miyake and Sugimura, 1969; Miyake et al., 1974; Roos and Gravenhorst, 1984). The general pattern of pCO_2 distribution in the surface sea water indicates that the water is supersaturated with respect to the pCO_2 in the air in the equatorial region, and undersaturated in the subtropics apart from in upwelling areas. However, little is known of the short- and long-

term variabilities of the ocean CO_2 (Weiss et al., 1982; Takahashi et al., 1983), in contrast with the variation in the atmospheric CO_2 concentration.

Because the $\delta^{13}C$ of CO_2 produced by fossil fuel combustion is much lower (about 17‰) than that of the atmospheric CO_2 (−8‰), a long-term decrease in the carbon isotope ratio takes place with the increase in the concentration in the air. However, the change in $\delta^{13}C$ corresponding to the rising concentration of atmospheric CO_2 is very different from the simple mixing of fossil fuel CO_2 with atmospheric CO_2 (Keeling et al., 1979; Mook et al., 1983; Keeling et al., 1984).

Air/sea exchange of CO_2 leads to a different relationship between concentration and carbon isotope ratio of atmospheric CO_2 than that achieved by the simple mixing of two different carbon isotopic species. We recently pointed out the importance of the kinetic isotope fractionation process as a possible cause of isotopic disequilibrium between air and sea water (Inoue and Sugimura, 1985a).

Precise and repeated measurements in the same area are now necessitated for the establishment of the long-term trend of pCO_2 and $\delta^{13}C$ of CO_2 in the air and surface sea water. Here we report the results of a study of the pCO_2 and $\delta^{13}C$ of atmospheric CO_2 and of surface sea water in the western North Pacific undertaken during a period from 1981 to 1985 for the purpose of detecting the long-term trend. Seasonal variation of pCO_2 in the surface sea water is also given for the area south of Japan.

2. Samples and analytical method

Measurements of the pCO_2 in the air and in the surface sea water were carried out from 1981 on board the R.V. Ryofu-maru belonging to the Japan Meteorological Agency, and on board the R.V. Hakuho-maru belonging to the Ocean Research Institute, University of Tokyo. In 1982 and 83, CO_2 was extracted from air and sea water samples on board in order to measure the carbon isotope ratio. In 1985, air and water samples were collected on board and the extraction of CO_2 was performed in the laboratory at Tsukuba. The ship tracks of the R.V. Ryofu-maru and Hakuho-maru are shown in Figs. 1, 2. The pCO_2 in the air and surface sea water was measured throughout the cruise and samples for carbon isotopic measurement were collected intermittently. The area studied for the seasonal variation of pCO_2 in the surface sea water is shown by a broken line in Fig. 2.

2.1. *Measurement of the pCO_2*

A schematic drawing of the instrument used for the determination of pCO_2 in the surface sea water and in the air is shown in Fig. 3. The system is essentially the same as that used in previous works (Miyake and Sugimura, 1969; Miyake et al., 1974; Inoue and Sugimura, 1985b), although a slight modification was made for the R.V. Hakuho-maru cruise (KH8503).

Sea water was pumped up continuously from the bottom of the ship (about 5 m below the surface) and introduced into an equilibrator. A constant volume of air (2 l) was circulated counter-currentwise in a closed circuit consisting of a small diaphragm pump, an electric dehumidifier, chemical desiccant ($Mg(ClO_4)_2$) and a non-dispersive infra-red gas analyzer (NDIR, Beckman Model 315A).

Correction was made for the observed pCO_2 in the surface water using eq. (1), due to a tempera-

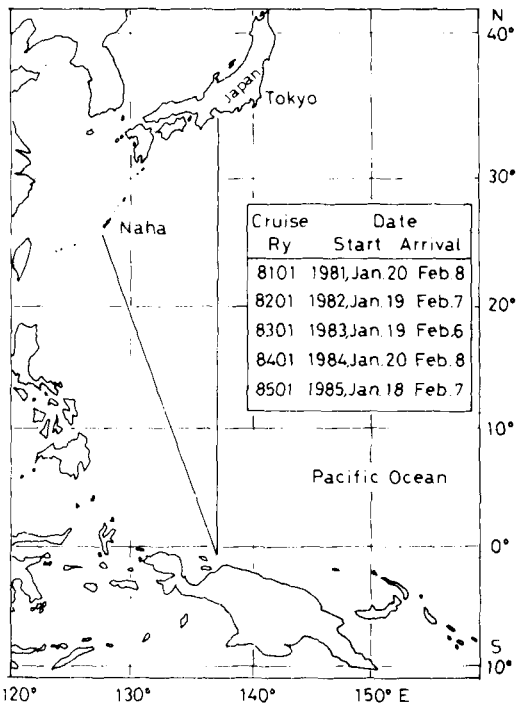

Fig. 1. Cruise track of the R.V. Ryofu-maru (Ry).

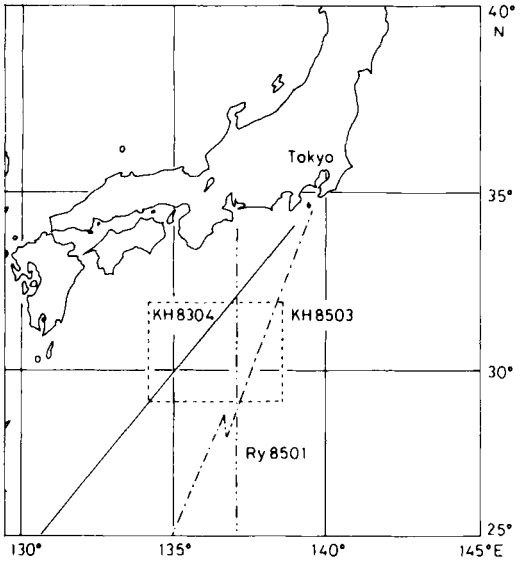

Fig. 2. Cruise tracks of the R.V. Ryofu-maru and R.V. Hakuho-maru (KH). Seasonality of the pCO_2 in the surface sea water was studied in the area enclosed by the broken line. pCO_2 was measured on January 19, 1985 (Ry8501), February 22, 1983 (KH8304) and June 29, 1985 (KH8503).

ture rise in the inner piping (Gordon and Jones, 1973):

$$\frac{\delta pCO_2}{\delta T} = 4.4 \times 10^{-2}(pCO_2) - 4.6 \times 10^{-6}(pCO_2)^2, \quad (1)$$

where T is the water temperature.

Air samples were obtained from an air inlet installed on the bow or windward of the ship with a rate of 5–10 l min^{-1}. 0.5 l min^{-1} of the air was passed through the NDIR's sample cell after removal of water vapor through the electrical and chemical desiccant system.

Four different concentrations (450, 380, 330, 250 ppm of CO_2 in N_2) of working standard gases were used to calibrate the instrument. Each working standard gas was passed through the sample cell for five minutes every hour in order to convert output voltage to concentration. The working standard gases were calibrated against the primary standard (CO_2 in air) prepared by the gravimetric method. The standard was standardized against the WMO standard (1981 mole fraction, supplied from the Scripps Institution of

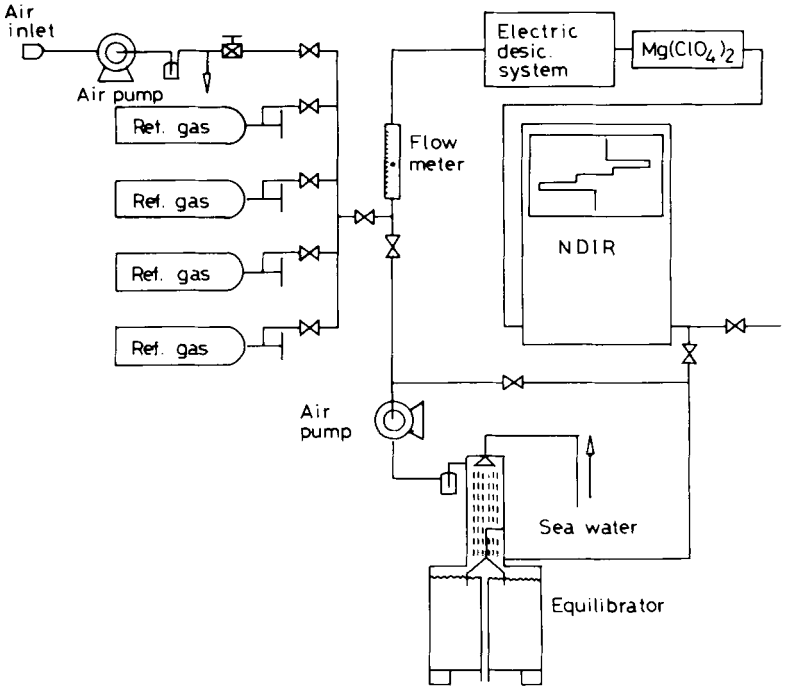

Fig. 3. Schematic diagram of air and surface sea water CO_2 measurement system.

Oceanography). A duplicate analysis of the same air revealed that the standard deviation of the analytical results is within ± 0.3 ppm in the laboratory on land and a little larger (0.4 to 0.5 ppm) during shipboard analysis.

2.2. *Measurement of the $\delta^{13}C$ of CO_2*

Sea water: total dissolved inorganic carbon ($\sum CO_2$) was extracted from a sea water sample in a portable vacuum line as described in a previous paper (Inoue and Sugimura, 1985a). In 1982 and 83, sample CO_2 was extracted and collected on board in a sample tube with a groundglass stopcock lubricated with Apiezon grease. The small amount of water vapor contained in the sample gas was completely removed in the laboratory at Tsukuba by the cryogenic distillation method (at 173 K).

In 1985, samples of surface sea water were collected together with some of deep sea water. The samples were sterilized by the addition of sodium azide (NaN_3) in a 100 ml polyethylene bottle (50 μg ml^{-1}) and stored in a deep freeze until the CO_2 was extracted in the Tsukuba laboratory. The results of our experiment into the $\delta^{13}C$ of the $\sum CO_2$ in deep sea water, however, will be given elsewhere.

Air: During the 82 and 83 cruises, sample air was collected in a plastic bag and the pCO_2 was continuously monitored on board. Within a few hours after sampling, CO_2 was extracted from the air and transferred into a sample tube using a portable shipboard vacuum line (Inoue and Sugimura, 1985a).

In 1985, air samples were collected in the same manner in 5 l elongated flasks (Pyrex glass, 130 mm dia) with teflon O-ring stopcocks at both ends. The flasks were evacuated and refilled with pure nitrogen (99.999%) before use. At the sampling, the inside of the flask was flushed with filtered air (Millipore 0.45 μm), while the concentration of CO_2 was continuously monitored on the NDIR, and finally the air sample was sealed in the flask at positive pressure, attained by first closing the outlet and then the inlet after confirmation of increased inside pressure to an optimum condition (1.2 to 1.4 kg cm^{-2}).

Measurement of the $^{13}C/^{12}C$ ratio of CO_2 in one sample was carried out within a few months after the collection, and it was confirmed that there was no change in the isotopic ratio during storage.

In the Tsukuba laboratory, the concentration of CO_2 in the air sample flasks was analyzed on NDIR (Beckman Model 864) and the CO_2 in the sample air was then extracted using a vacuum manifold line. The flask was installed in the vacuum line, and the air in the flask was circulated through a large spherical liquid nitrogen trap filled with Dixon Packing (1.5 mm) by a Toepler pump (Misuzu Co. Ltd.), at a flow rate of 1 l min^{-1} at STP in a closed circuit. After total extraction, the CO_2 in the trap was transferred into a sample tube for the purpose of mass spectrometry.

It has been confirmed that there is no difference in the value of carbon isotopic ratio due to the different techniques used at sea and on land (Inoue and Sugimura, 1985b, c).

The isotopic composition of carbon in the CO_2 was measured on a triple ion collector mass spectrometer (Finnigan MAT 250). The result is expressed as the per-mil deviation from the PDB standard:

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_{\text{sample}}}{(^{13}C/^{12}C)_{\text{PDB}}} - 1 \right] \times 10^3; \qquad (2)$$

NBS-20, NBS-19, NBS-18, NBS-17 and NBS-16 obtained from the US National Bureau of Standards are in use together with four laboratory isotopic standards. To detect the long-term trend of $\delta^{13}C$ in a natural system, sufficient stability of the mass spectrometer is required (Mook et al., 1983). For this purpose, stability of our instrument is maintained within an accuracy of ± 0.05‰ with respect to NBS-20 for 5 years.

Corrections due to N_2O which is trapped with CO_2 and interferes with the isotope measurement (Mook and Van der Hoek, 1983) does not apply to this report. On our mass spectrometer, the beam intensity of mass 44 ion of N_2O^+ is about 71% to that of CO_2^+ at an equal inlet pressure (Inoue and Sugimura, 1985c). Considering the background concentration of N_2O (Weiss, 1981), we propose the addition of +0.23‰ to our $\delta^{13}C$ value in this report (Craig and Keeling, 1963).

2.3. *Data selection of the pCO_2 and $\delta^{13}C$*

2.3.1. pCO_2 of atmospheric CO_2. Data with short-term fluctuations with periodicities from

seconds to several minutes was excluded from the continuous record of the atmospheric CO_2 concentration as artifact such as exhaust from the ship. For the calculation of background CO_2 concentration in the air over the open western North Pacific south of 30°N, data was selected so as to be within ± 1 sigma (standard deviation) of the mean value at each latitudinal zone. This criterion does not apply to the data in the air north of 30°N, due to a prevailing northwest wind from the Japanese islands where the concentration of atmospheric CO_2 is greatly affected by the land biota and human activities. The impact of data selection on the shipboard record depends strongly not only on the stability of electric power and temperature of the cell, but also on the weather during a cruise. Our selection scheme removed 17% of the total data gleaned in 1981, 18% for 1982, 20% for 1983, 27% for 1984 and 17% for 1985. The difference in the mean values between selected and total data set in the south of 30°N is in a range between 0 ppm and 0.8 ppm.

2.3.2. pCO_2 in the surface sea water. Data selection must be carried out with care, because pCO_2 in the surface sea water exhibits great variability. After examination of the data with respect to oceanographic parameters, some data was excluded as unrepresentative. Such examples were caused by fluctuations of output voltage during rough weather, undesirable contamination from room air, air circulation pump malfunction, careless use of an adhesive agent which interferes with the measurement, and so on. Our selection scheme removed 19% of the total data gleaned in 1981, 3% for 1982, 12% for 1983, 10% for 1984 and 3% for 1985.

2.3.3. $\delta^{13}C$ of atmospheric CO_2 and of the $\sum CO_2$ in sea water. Extractions of CO_2 for the purpose of $\delta^{13}C$ measurements were taken from 12 air samples and 11 sea water samples in 1982, 13 and 13 in 1983, and 13 and 17 in 1985. Of the 79 samples, the results of 72 are given in this report. The results of 7 samples have been excluded, because 3 were lost during sample tube handling, 2 in imposed variation in preparation of samples for mass spectrometry and 2 during improper sterilization. Because the concentration of CO_2 in the air sample collected in a glass flask on board is in the range of ± 0.6 ppm of the record at the same sampling station, it has been decided that no loss or gain of CO_2 occurred in the sample air during storage.

3. Results and discussion

Although variations in the pCO_2 in the air have been analyzed in terms of various periodicities (Spittlehouse and Ripley, 1977; Halter and Harris, 1983), those in the surface sea water remain undetermined. Recently, Keeling pointed out an approximately parallel increase of the pCO_2 in surface sea water in the Sargasso Sea with that in the atmospheric CO_2 record at Mauna Loa Observatory (Keeling, 1985 personal communication; Takahashi et al., 1983). Because of the long-term variation in the pCO_2 in the surface sea water is relatively small and generally modified or overridden by changes in biological fixation and/or seasonal temperature, the short-term variation should be characterized in order to ascertain the long-term trend of pCO_2.

Distribution in pCO_2 and $\delta^{13}C$ of atmospheric CO_2 gives an information concerning the origin of CO_2 added to and/or extracted from the air. And long-term variation in the relationship between pCO_2 and $\delta^{13}C$ of atmospheric CO_2 can be used to distinguish between air/sea and air/biosphere CO_2 exchange. Therefore this paper records activities concerning the time and spatial variation in pCO_2 and $\delta^{13}C$ of CO_2 observed in and over the western North Pacific during the period from 1981 to 1985.

3.1. Distribution of pCO_2 in surface sea water

The meridional distributions of the pCO_2 in the surface sea water are shown in Figs. 4, 5 for the area from 35°N to 1°S, along 137°E and from 1°S 137°E to 25°N 128°E. Average values of pCO_2 in the surface sea water at each latitude are summarized in Tables 1, 2. The general pattern of distribution is almost the same as that mentioned in previous papers (Keeling, 1968; Akiyama, 1968; Miyake and Sugimura, 1969; Miyake et al., 1974), but the pCO_2 is 10 to 20 ppm higher than the previous value. As seen in these Figures, the pCO_2 in the surface sea water is high in the coastal area off Japan and in the equatorial region, and low in the subtropical gyre. The partial pressure changed slightly every year at the Kuroshio Front located around 32.5°N, irrespec-

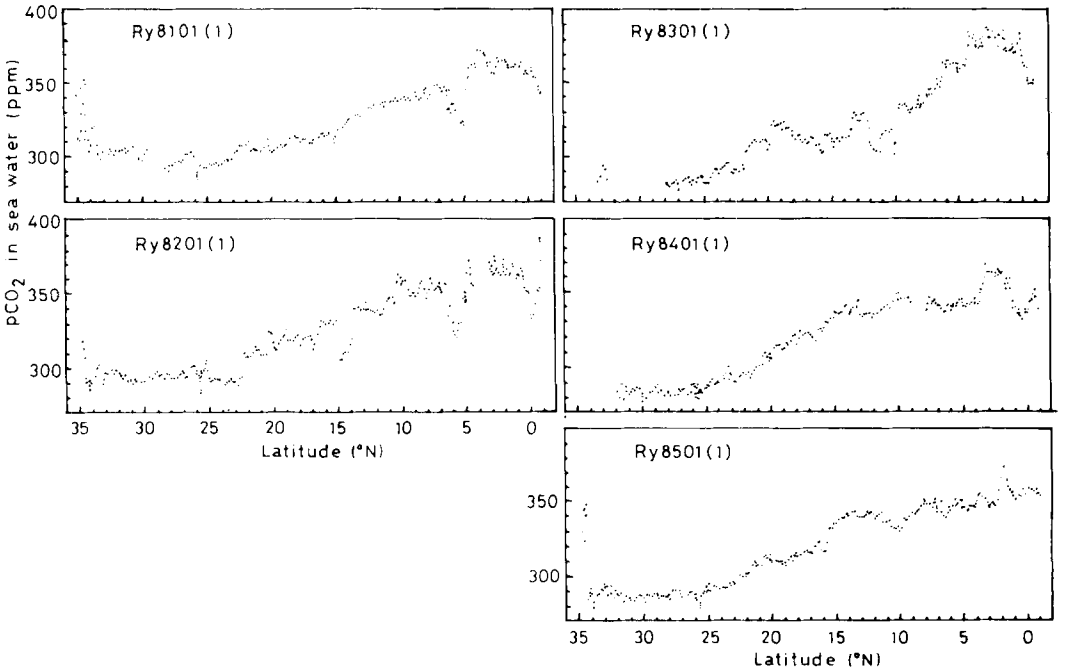

Fig. 4. Meridional distribution of pCO_2 in the surface sea water for the period from 1981 to 1985. Numeral 1 in parentheses represents the southward transect from the Japanese islands to the equator along 137°E.

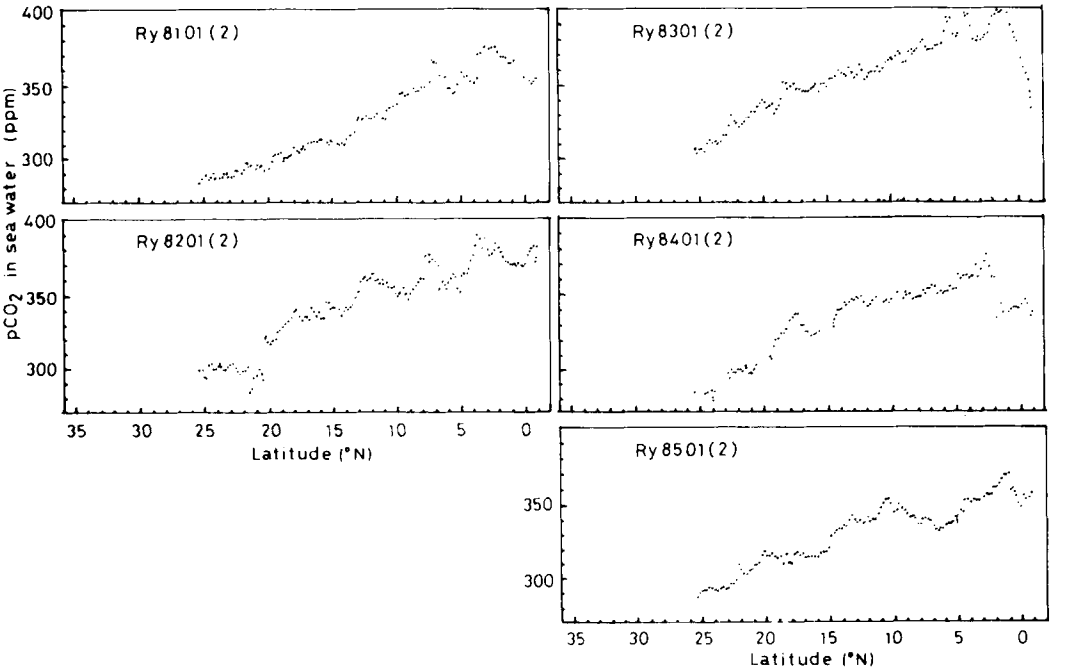

Fig. 5. Meridional distribution of pCO_2 in the surface sea water for the period from 1981 to 1985. Numeral 2 in parentheses represents the northward transect from the equator to Naha.

tive of temperature differences (Inoue and Sugimura, 1985b). The highest value of pCO_2 in the surface sea water was observed in the South Equatorial current (2°N to 4°N), ranging from 356.6 ppm to 390.7 ppm, while the lowest is in the temperate zone (26°N to 31°N), with values of 282.5 ppm to 290.7 ppm.

The El Niño Event in 1982/83 significantly modified the distribution of temperature and pCO_2 in the waters south of 17°N in the western North Pacific. The partial pressure of CO_2 in the surface sea water in the area from 7°N to 1°S along 137°E and from 1°S 137°E to 15°N 131°30′E increased with the temperature decrease, whereas waters in the North Equatorial current, from 17°N to 7°N along 137°E, showed a decrease in pCO_2 with the temperature decrease. During the El Niño Event, the apparent temperature dependent of pCO_2 in the surface sea water between 17°N to 7°N along 137°E was about two times more than that estimated by eq. (1). The discrepancy of the relationship between pCO_2 and water temperature in these two regions can be explained by the fact that the former is caused by enhanced upwelling in the western North Pacific by the displacement of warm surface water to the east (Fushimi, 1986). The southward shift of the surface waters around 17°N (North Equatorial current) would seem to be one of the causes of this since pCO_2 and temperature observed around 17°N usually fall in relatively narrow ranges (310–320 ppm, 26–27°C) every year except for the year of the El Niño Event. In 1983, the area was spread southward to 10°N and the pCO_2 and temperature became remarkably low in this region. No significant difference in the pCO_2–T relationship was observed in the water north of 17°N along 137°E, even in the year of the large El Niño Event.

As has already been pointed out (Miyake et al., 1974), the higher values of pCO_2 in the surface sea water in the South Equatorial current were essentially supported by the continuous upwelling of subsurface CO_2 gas rich water along the coast off South America and subsequent westward flow along the equator, and by the hydrographic structure. During the El Niño Event, the piled-up water in the west side of the equatorial Pacific moved eastward following the weakened east wind. The changing hydrographic structure significantly disturbed the pCO_2 distribution in the equatorial Pacific waters, and subsequently the air/sea exchange of CO_2 in the equatorial Pacific waters. The growth rate of atmospheric CO_2 during the El Niño Event cannot therefore be directly interpreted as the effects of temperature on pCO_2 in the sea water alone.

3.2. Short-term variation in pCO_2 in surface sea water

As seen in the previous section, yearly variation in the pCO_2 in the surface sea water is essentially controlled by the dynamic characteristic of the water. Within the same water mass and under the same meteorological conditions, the pCO_2 in the surface water should change with changes in water temperature and magnitude of biological activities.

Diurnal and seasonal variation in the pCO_2 in open ocean water has not been yet identified. Spectral analysis did not indicate clearly the presence of the diurnal variation due to biological effects. It appeared as a series of irregular hourly variations which sometimes span over several parts per million. The mean values in Tables 1, 2 are considered to be representative of water in winter in the western North Pacific, although a small diurnal variation and other periodicities may be present.

Seasonal variation in pCO_2 in the surface sea water was investigated in the area surrounded by the broken line in Fig. 2. The value of pCO_2 in the area is plotted against the latitude and surface sea water temperature as seen in Fig. 6. As seen in this Figure, pCO_2 in the surface sea water is high in summer and low in winter, with the seasonal difference at about 20 ppm.

The annual cycle of pCO_2 in surface sea water is quite different in phase from that in the air CO_2 in the northern hemisphere. The pCO_2 in the air of the northern hemisphere shows a sharp decrease during the period from late spring to early summer due to the biological fixation by land plants (Komhyr et al., 1985; Pearman et al., 1983; Bolin and Keeling, 1963). Moreover, the magnitude of the annual cycle of pCO in surface sea water is much larger than that in the air at approximately the same latitude (Komhyr et al., 1985; Bolin and Keeling, 1963; Fraser et al., 1983). The annual cycle of the pCO_2 in the surface sea water significantly affects the exchange of CO_2 between air and sea water.

Table 1. *Mean values of pCO_2 in the surface sea water in the western North Pacific*

	Ry8101 (1)		Ry8201 (1)		Ry8301 (1)		Ry8401 (1)		Ry8501 (1)	
Latitude	pCO_2 (ppm)	T (°C)	pCO_2 (ppm)	T (°C)	pCO_2 (ppm)	T (°C)	pCO_2 (ppm)	T (°C)	pCO_2 (ppm)	T (°C)
35°N	326.2 ± 13.9 (6)*	15.1 ± 1.2 (6)*	313.6 ± 5.0 (3)	15.6 ± 0.6 (3)					332.4 ± 9.1 (3)	14.4 ± 0.5 (5)
34	324.2 ± 15.1 (12)	14.6 ± 1.2 (14)	291.4 ± 3.5 (15)	17.1 ± 0.2 (15)					295.7 ± 22.2 (12)	16.6 ± 1.1 (12)
33	302.1 ± 3.1 (6)	19.1 ± 1.7 (7)	297.0 ± 4.8 (6)	16.9 ± 0.1 (7)	288.3 ± 4.2 (7)	19.1 ± 1.9 (7)			292.5 ± 2.2 (7)	17.9 ± 0.8 (7)
32	304.0 ± 1.6 (5)	19.0 ± 0.1 (6)	296.9 ± 2.0 (6)	18.3 ± 0.8 (6)			285.0 ± 3.8 (3)	20.5 ± 0.1 (3)	287.3 ± 2.5 (7)	20.4 ± 0.2 (7)
31	304.7 ± 1.7 (5)	19.0 ± 0.1 (7)	292.2 ± 2.2 (6)	19.9 ± 0.1 (6)			284.2 ± 2.2 (7)	19.8 ± 0.5 (7)	284.8 ± 1.0 (7)	19.8 ± 0.1 (7)
30	300.1 ± 2.9 (5)	19.1 ± 0.0 (7)	291.8 ± 0.9 (6)	19.6 ± 0.1 (7)			281.5 ± 3.2 (8)	19.9 ± 0.3 (9)	285.6 ± 1.7 (10)	19.8 ± 0.1 (10)
29			296.2 ± 1.8 (6)	19.8 ± 0.1 (6)			285.6 ± 1.8 (7)	19.7 ± 0.1 (7)	287.1 ± 1.3 (7)	20.3 ± 0.2 (7)
28	292.7 ± 1.2 (4)	19.6 ± 0.1 (6)	294.3 ± 1.2 (7)	20.3 ± 0.1 (7)	281.1 ± 1.1 (4)	21.6 ± 0.3 (7)	282.6 ± 1.2 (6)	20.6 ± 0.1 (6)	287.0 ± 2.3 (6)	20.7 ± 0.3 (6)
27	297.7 ± 1.9 (5)	20.3 ± 0.3 (6)	296.1 ± 1.2 (6)	20.6 ± 0.7 (6)	281.9 ± 2.8 (5)	22.2 ± 0.2 (6)	283.9 ± 1.4 (7)	20.8 ± 0.2 (7)	288.2 ± 1.9 (6)	20.7 ± 0.3 (7)
26	290.0 ± 5.9 (19)	21.0 ± 0.1 (23)	290.7 ± 7.4 (25)	21.0 ± 0.4 (25)	283.4 ± 1.8 (6)	21.8 ± 0.2 (6)	284.4 ± 3.2 (17)	21.1 ± 0.2 (17)	283.4 ± 3.8 (16)	21.1 ± 0.4 (16)
25	293.1 ± 1.1 (9)	21.3 ± 0.4 (11)	297.7 ± 4.8 (9)	21.9 ± 0.7 (9)	284.2 ± 1.8 (8)	22.3 ± 0.2 (8)	287.1 ± 3.0 (10)	22.5 ± 1.1 (12)	291.9 ± 1.9 (11)	22.9 ± 0.5 (11)
24	295.3 ± 1.1 (5)	22.1 ± 0.4 (6)	291.8 ± 1.5 (5)	23.8 ± 0.1 (5)	291.0 ± 1.5 (6)	22.4 ± 0.3 (3)	293.2 ± 4.9 (6)	21.9 ± 0.5 (6)	292.5 ± 0.5 (5)	24.1 ± 0.2 (7)
23	300.0 ± 2.6 (5)	23.2 ± 0.1 (6)	291.5 ± 1.8 (6)	23.9 ± 0.2 (6)	292.5 ± 3.0 (6)	23.0 ± 0.5 (6)	295.1 ± 3.7 (6)	23.6 ± 0.9 (7)	295.3 ± 2.5 (7)	23.8 ± 0.6 (7)
22	307.2 ± 1.9 (5)	22.9 ± 0.3 (6)	306.7 ± 5.7 (6)	23.9 ± 0.1 (6)	295.8 ± 5.8 (6)	24.8 ± 0.5 (6)	296.3 ± 1.2 (6)	23.9 ± 0.2 (6)	302.3 ± 2.8 (6)	24.8 ± 0.3 (7)
21	304.1 ± 0.5 (4)	23.6 ± 0.2 (5)	311.3 ± 2.5 (6)	24.3 ± 0.1 (6)	309.8 ± 1.3 (7)	25.8 ± 0.1 (7)	300.1 ± 4.5 (7)	24.8 ± 0.6 (7)	309.0 ± 2.0 (6)	25.9 ± 0.3 (6)
20	305.6 ± 3.0 (6)	24.2 ± 0.1 (8)	318.0 ± 4.8 (8)	25.5 ± 0.3 (8)	312.8 ± 6.3 (8)	26.1 ± 0.3 (8)	308.2 ± 2.8 (9)	25.8 ± 0.2 (9)	311.3 ± 1.6 (7)	26.1 ± 0.1 (8)
19	307.9 ± 2.1 (7)	25.1 ± 0.5 (7)	320.7 ± 2.7 (6)	26.1 ± 0.0 (6)	321.1 ± 1.8 (5)	26.4 ± 0.0 (6)	313.9 ± 1.5 (6)	26.2 ± 0.1 (6)	308.9 ± 1.4 (6)	26.1 ± 0.1 (6)
18	312.2 ± 1.5 (4)	25.9 ± 0.0 (5)	320.0 ± 2.4 (6)	26.1 ± 0.1 (6)	315.6 ± 2.5 (9)	26.4 ± 0.0 (9)	319.3 ± 3.1 (6)	26.3 ± 0.1 (6)	313.5 ± 2.0 (7)	26.7 ± 0.2 (7)
17	309.9 ± 1.1 (5)	26.1 ± 0.1 (6)	319.2 ± 3.3 (7)	26.7 ± 0.2 (7)	310.9 ± 1.5 (6)	26.6 ± 0.2 (6)	320.9 ± 1.2 (6)	26.4 ± 0.1 (6)	316.4 ± 1.6 (6)	26.9 ± 0.2 (6)
16	314.2 ± 1.0 (5)	26.7 ± 0.1 (6)	330.0 ± 1.3 (5)	27.3 ± 0.2 (5)	306.0 ± 3.5 (6)	26.8 ± 0.0 (6)	324.3 ± 3.7 (6)	27.1 ± 0.3 (6)	320.0 ± 3.2 (6)	27.2 ± 0.1 (6)
15	313.1 ± 2.7 (6)	26.8 ± 0.2 (8)	321.9 ± 11.6 (8)	27.3 ± 0.1 (8)	311.3 ± 2.9 (10)	26.7 ± 0.1 (10)	333.9 ± 2.3 (8)	27.9 ± 0.2 (8)	334.8 ± 2.1 (9)	27.5 ± 0.1 (9)
14	322.9 ± 2.1 (5)	27.6 ± 0.1 (6)	322.4 ± 12.4 (6)	28.0 ± 0.3 (6)	313.5 ± 2.3 (6)	26.6 ± 0.1 (6)	337.4 ± 2.5 (7)	28.1 ± 0.2 (7)	340.6 ± 1.3 (6)	27.9 ± 0.0 (6)
13	328.1 ± 0.7 (5)	28.0 ± 0.1 (6)	340.0 ± 1.7 (6)	28.3 ± 0.1 (6)	326.8 ± 2.2 (6)	27.2 ± 0.2 (6)	337.7 ± 4.2 (6)	28.2 ± 0.1 (6)	339.9 ± 1.4 (6)	28.0 ± 0.0 (6)
12	333.3 ± 1.0 (5)	28.0 ± 0.0 (6)	336.9 ± 1.2 (6)	28.4 ± 0.1 (6)	313.9 ± 9.1 (7)	26.9 ± 0.1 (7)	334.2 ± 1.1 (6)	28.2 ± 0.0 (6)	341.3 ± 1.5 (7)	28.1 ± 0.0 (7)
11	335.7 ± 1.5 (5)	28.1 ± 0.0 (6)	344.3 ± 2.9 (6)	28.6 ± 0.2 (6)	310.8 ± 6.0 (5)	26.9 ± 0.1 (5)	339.1 ± 2.1 (7)	28.5 ± 0.1 (7)	336.9 ± 2.7 (6)	28.0 ± 0.1 (6)
10	338.2 ± 1.1 (6)	28.1 ± 0.1 (7)	358.6 ± 2.4 (7)	29.1 ± 0.3 (6)	318.9 ± 12.1 (6)	27.0 ± 0.1 (8)	347.6 ± 2.6 (9)	28.2 ± 2.6 (9)	332.5 ± 2.4 (9)	27.8 ± 0.1 (9)
9	339.4 ± 1.8 (5)	28.2 ± 0.2 (6)	350.6 ± 3.0 (8)	28.8 ± 0.1 (8)	332.6 ± 2.0 (6)	27.6 ± 0.0 (6)	344.5 ± 1.5 (3)	28.4 ± 0.0 (7)	340.9 ± 2.2 (7)	27.8 ± 0.0 (7)
8	341.9 ± 2.7 (8)	28.2 ± 0.1 (9)	354.2 ± 4.3 (8)	28.8 ± 0.1 (8)	335.2 ± 2.7 (9)	27.5 ± 0.1 (9)	341.7 ± 3.6 (3)	28.6 ± 0.2 (10)	348.6 ± 1.7 (9)	28.3 ± 0.1 (9)
7	346.7 ± 1.3 (6)	28.4 ± 0.2 (8)	353.4 ± 2.4 (8)	28.7 ± 0.1 (8)	344.7 ± 3.4 (10)	27.7 ± 0.1 (10)	341.9 ± 2.1 (10)	28.9 ± 0.0 (10)	346.6 ± 3.5 (7)	27.9 ± 0.3 (8)
6	335.1 ± 5.2 (9)	27.5 ± 0.2 (10)	331.9 ± 10.4 (11)	27.9 ± 0.5 (11)	360.0 ± 6.8 (10)	27.8 ± 0.1 (10)	339.1 ± 2.1 (10)	28.8 ± 0.0 (10)	345.4 ± 3.7 (12)	28.3 ± 0.1 (12)
5	337.3 ± 15.9 (10)	27.7 ± 0.2 (12)	351.1 ± 11.5 (13)	28.3 ± 0.2 (13)	361.0 ± 2.4 (13)	27.8 ± 0.0 (13)	342.4 ± 1.8 (16)	28.5 ± 0.2 (16)	346.6 ± 2.1 (15)	28.4 ± 0.1 (15)
4	364.0 ± 4.2 (6)	28.3 ± 0.1 (8)	354.9 ± 0.7 (2)	28.6 ± 0.1 (11)	377.9 ± 8.1 (8)	28.0 ± 0.1 (8)	343.9 ± 3.1 (11)	28.1 ± 0.1 (12)	352.9 ± 7.2 (12)	29.1 ± 0.3 (12)
3	366.0 ± 4.9 (8)	28.7 ± 0.1 (10)	367.3 ± 4.4 (9)	29.1 ± 0.1 (12)	378.6 ± 4.5 (13)	28.0 ± 0.1 (13)	362.2 ± 4.3 (12)	28.2 ± 0.1 (12)	349.2 ± 2.2 (12)	29.0 ± 0.2 (12)
2	363.3 ± 3.3 (9)	29.2 ± 0.1 (10)	365.3 ± 3.2 (12)	29.1 ± 0.1 (12)	381.3 ± 3.5 (11)	28.4 ± 0.1 (12)	360.2 ± 3.8 (12)	28.7 ± 0.4 (12)	356.6 ± 10.1 (8)	29.2 ± 0.4 (12)
1	361.9 ± 0.8 (5)	28.7 ± 0.1 (11)	364.4 ± 3.6 (8)	28.9 ± 0.1 (8)	375.0 ± 4.5 (11)	28.3 ± 0.0 (11)	341.8 ± 8.4 (12)	29.6 ± 0.1 (12)	356.1 ± 4.3 (12)	28.6 ± 0.2 (12)
0	357.7 ± 3.1 (10)	28.8 ± 0.1 (12)	345.9 ± 10.6 (15)	28.4 ± 0.1 (15)	372.4 ± 6.0 (12)	28.5 ± 0.1 (12)	337.9 ± 5.0 (12)	29.7 ± 0.1 (15)	356.0 ± 2.8 (10)	28.4 ± 0.0 (15)
1°S	347.8 ± 4.9 (9)	28.5 ± 0.2 (12)	370.8 ± 13.9 (13)	28.5 ± 0.3 (13)	350.1 ± 7.1 (13)	28.5 ± 0.1 (13)	340.8 ± 5.2 (8)	29.6 ± 0.2 (8)	355.6 ± 1.7 (10)	28.6 ± 0.2 (10)

* Data is presented along with 1 σ; numerals in parentheses are the number of measurements.

Table 2. *Mean values of pCO_2 in the surface sea water in the western North Pacific*

	Ry8101 (2)		Ry8201 (2)		Ry8301 (2)		Ry8401 (2)		Ry8501 (2)	
Latitude	pCO_2 (ppm)	T (°C)	pCO_2 (ppm)	T (°C)	pCO_2 (ppm)	T (°C)	pCO_2 (ppm)	T (°C)	pCO_2 (ppm)	T (°C)
25°N	285.9 ± 1.7 (4)*	21.6 ± 0.8 (3)*	297.5 ± 3.4 (5)	21.9 ± 0.1 (5)	305.2 ± 1.2 (5)	21.9 ± 0.7 (5)	284.7 ± 0.9 (2)	21.7 ± 0.2 (6)	291.0 ± 1.9 (5)	21.4 ± 0.1 (5)
24	287.3 ± 1.1 (5)	22.3 ± 0.0 (2)	300.3 ± 1.5 (6)	21.8 ± 0.3 (6)	310.8 ± 1.2 (5)	23.4 ± 0.7 (5)	282.8 ± 2.6 (6)	21.7 ± 0.6 (9)	293.2 ± 1.1 (5)	22.1 ± 0.4 (5)
23	289.0 ± 1.5 (6)	23.0 ± 0.3 (7)	300.9 ± 1.4 (5)	22.3 ± 0.2 (5)	316.4 ± 4.0 (4)	24.5 ± 0.4 (4)	296.8 ± 2.2 (3)	24.0 ± 0.2 (6)	294.6 ± 1.2 (5)	22.7 ± 0.4 (5)
22	292.7 ± 2.8 (4)	23.0 ± 0.4 (5)	298.5 ± 1.3 (5)	22.0 ± 0.2 (5)	324.8 ± 2.9 (5)	25.3 ± 0.2 (5)	299.0 ± 0.9 (6)	24.0 ± 0.0 (6)	304.2 ± 3.7 (5)	24.6 ± 0.6 (5)
21	294.6 ± 1.0 (5)	23.7 ± 0.3 (6)	292.6 ± 5.5 (6)	23.0 ± 0.8 (6)	329.1 ± 2.6 (5)	25.5 ± 0.1 (5)	299.3 ± 2.3 (7)	23.7 ± 0.2 (7)	308.4 ± 2.0 (5)	24.9 ± 0.2 (5)
20	295.8 ± 3.8 (5)	24.7 ± 0.6 (6)	314.1 ± 11.1 (5)	24.5 ± 0.2 (5)	337.7 ± 1.9 (5)	25.3 ± 0.1 (5)	309.3 ± 0.0 (2)	23.9 ± 0.5 (8)	316.6 ± 0.9 (4)	25.7 ± 0.1 (4)
19	300.3 ± 1.6 (13)	25.2 ± 0.2 (16)	326.6 ± 3.7 (5)	25.8 ± 0.5 (5)	334.7 ± 2.1 (5)	25.2 ± 0.1 (5)	317.3 ± 5.9 (5)	26.0 ± 0.4 (5)	314.1 ± 2.7 (5)	25.6 ± 0.2 (5)
18	303.8 ± 2.3 (6)	25.3 ± 0.1 (7)	336.6 ± 2.9 (5)	26.6 ± 0.0 (5)	348.3 ± 4.2 (5)	26.3 ± 0.6 (5)	330.0 ± 4.0 (4)	26.8 ± 0.1 (4)	313.9 ± 3.0 (4)	25.6 ± 0.2 (4)
17	308.3 ± 1.6 (4)	25.4 ± 0.1 (5)	336.1 ± 3.0 (5)	26.6 ± 0.0 (5)	347.3 ± 1.8 (5)	26.9 ± 0.1 (5)	331.7 ± 4.6 (5)	26.8 ± 0.2 (5)	316.2 ± 1.5 (5)	25.8 ± 0.1 (5)
16	311.9 ± 0.9 (5)	26.2 ± 0.3 (6)	336.9 ± 2.0 (5)	26.6 ± 0.0 (5)	347.3 ± 2.1 (5)	27.0 ± 0.0 (5)	324.5 ± 1.3 (5)	26.5 ± 0.3 (5)	316.2 ± 1.3 (5)	26.0 ± 0.2 (5)
15	311.0 ± 1.1 (5)	26.4 ± 0.0 (6)	343.4 ± 2.0 (5)	26.7 ± 0.0 (5)	350.8 ± 2.0 (4)	27.0 ± 0.0 (4)	331.3 ± 1.9 (4)	27.2 ± 0.3 (8)	324.8 ± 5.2 (4)	26.7 ± 0.4 (4)
14	310.7 ± 1.2 (4)	26.7 ± 0.3 (5)	339.9 ± 2.1 (5)	27.0 ± 0.3 (5)	356.9 ± 1.5 (5)	27.2 ± 0.0 (5)	339.7 ± 2.8 (5)	27.9 ± 0.1 (5)	335.2 ± 1.4 (5)	27.8 ± 0.1 (5)
13	323.8 ± 5.3 (5)	27.5 ± 0.1 (5)	350.8 ± 6.7 (6)	27.4 ± 0.3 (6)	356.8 ± 2.8 (4)	27.1 ± 0.0 (4)	345.5 ± 1.9 (5)	28.2 ± 0.0 (5)	340.4 ± 1.4 (5)	28.0 ± 0.0 (5)
12	328.8 ± 0.4 (4)	27.6 ± 0.0 (5)	361.1 ± 1.4 (5)	28.1 ± 0.1 (5)	357.4 ± 3.3 (6)	27.2 ± 0.1 (6)	345.0 ± 2.2 (5)	28.0 ± 0.1 (5)	339.6 ± 1.2 (5)	28.1 ± 0.0 (5)
11	329.8 ± 2.5 (4)	27.8 ± 0.2 (5)	357.7 ± 1.6 (6)	28.1 ± 0.1 (6)	359.4 ± 1.6 (4)	27.4 ± 0.1 (4)	346.1 ± 1.2 (5)	28.2 ± 0.1 (6)	345.9 ± 4.1 (4)	28.0 ± 0.1 (4)
10	337.8 ± 4.0 (4)	27.9 ± 0.2 (5)	352.6 ± 2.2 (5)	28.2 ± 0.0 (5)	364.8 ± 2.1 (5)	27.6 ± 0.1 (5)	346.1 ± 0.9 (2)	28.5 ± 0.1 (2)	349.9 ± 3.7 (5)	27.9 ± 0.1 (5)
9	345.1 ± 1.6 (4)	28.1 ± 0.1 (5)	351.6 ± 2.9 (5)	28.5 ± 0.1 (5)	366.6 ± 2.9 (5)	27.8 ± 0.1 (5)	349.6 ± 2.0 (4)	28.2 ± 0.2 (4)	346.1 ± 3.2 (5)	27.9 ± 0.0 (5)
8	347.6 ± 1.2 (4)	28.3 ± 0.1 (5)	362.4 ± 7.0 (5)	29.0 ± 0.1 (5)	371.6 ± 1.1 (5)	27.8 ± 0.1 (5)	347.8 ± 1.0 (5)	28.2 ± 0.0 (5)	339.6 ± 1.9 (5)	27.9 ± 0.0 (5)
7	361.4 ± 5.8 (5)	27.9 ± 0.2 (5)	372.8 ± 2.4 (5)	29.2 ± 0.1 (5)	375.3 ± 2.9 (5)	27.7 ± 0.2 (5)	353.3 ± 1.7 (5)	28.2 ± 0.1 (5)	338.6 ± 2.6 (5)	28.0 ± 0.0 (5)
6	348.5 ± 3.8 (4)	27.8 ± 0.1 (5)	357.4 ± 2.4 (6)	28.6 ± 0.2 (6)	377.0 ± 3.9 (5)	28.0 ± 0.1 (5)	351.5 ± 1.8 (6)	27.8 ± 0.1 (6)	335.4 ± 1.6 (5)	28.1 ± 0.1 (5)
5	352.3 ± 5.1 (4)	27.9 ± 0.0 (5)	359.6 ± 5.0 (6)	28.7 ± 0.0 (6)	388.3 ± 5.4 (5)	27.7 ± 0.1 (5)	356.5 ± 4.1 (4)	27.8 ± 0.0 (4)	340.3 ± 2.9 (11)	28.4 ± 0.1 (11)
4	353.6 ± 1.5 (4)	28.1 ± 0.2 (5)	372.6 ± 7.0 (5)	28.9 ± 0.2 (5)	390.7 ± 4.7 (5)	28.0 ± 0.1 (11)	361.5 ± 0.8 (5)	28.2 ± 0.3 (5)	351.4 ± 3.0 (5)	28.6 ± 0.1 (5)
3	372.9 ± 2.4 (4)	28.6 ± 0.2 (5)	382.4 ± 4.2 (5)	29.3 ± 0.2 (5)	379.6 ± 1.0 (5)	28.0 ± 0.0 (5)	367.0 ± 3.8 (4)	29.1 ± 0.3 (4)	354.4 ± 1.4 (4)	28.8 ± 0.0 (4)
2	373.1 ± 2.4 (4)	28.9 ± 0.0 (5)	379.3 ± 3.4 (6)	29.3 ± 0.1 (6)	386.8 ± 4.8 (4)	28.3 ± 0.0 (5)	359.9 ± 14.4 (5)	30.0 ± 0.1 (5)	359.3 ± 2.7 (5)	28.7 ± 0.0 (5)
1	366.6 ± 1.6 (5)	28.6 ± 0.1 (5)	371.1 ± 0.7 (5)	29.0 ± 0.1 (5)			339.8 ± 2.3 (4)	29.4 ± 0.2 (5)	367.1 ± 3.7 (5)	28.9 ± 0.2 (5)
0	354.4 ± 1.6 (2)	28.6 ± 0.0 (3)	371.1 ± 2.5 (6)	28.9 ± 0.0 (6)	379.7 ± 7.4 (5)	28.3 ± 0.1 (5)	342.1 ± 2.2 (5)	29.5 ± 0.0 (5)	352.9 ± 3.8 (5)	28.6 ± 0.1 (5)

* Data is presented along with 1 σ; numerals in parentheses are the number of measurements.

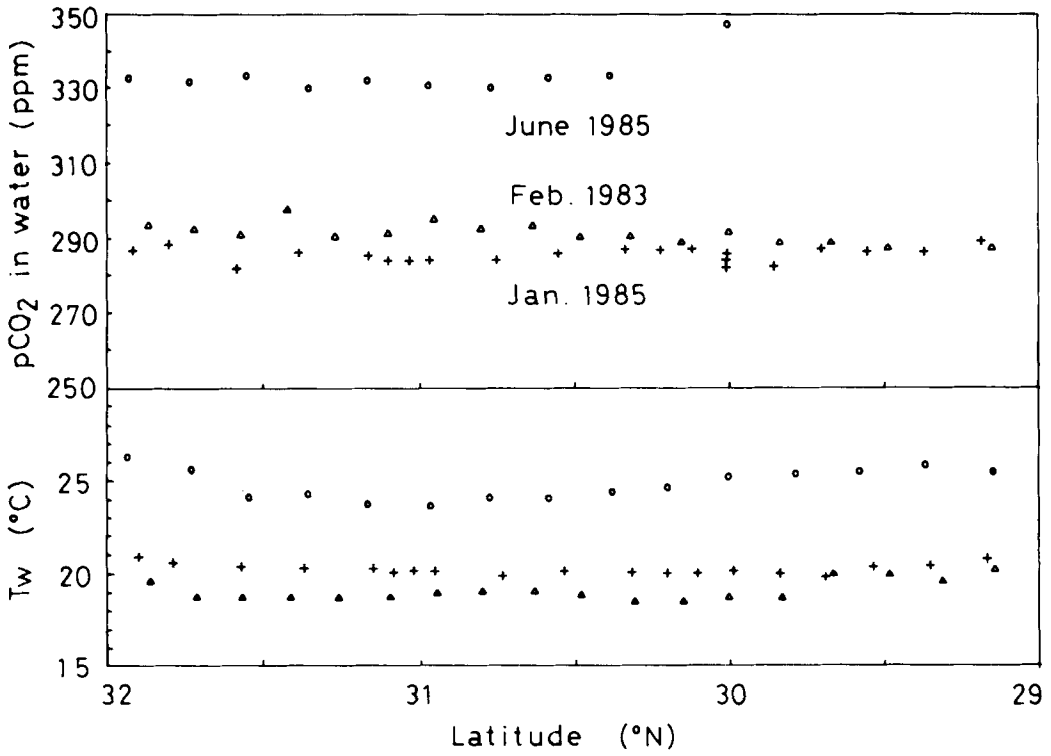

Fig. 6. Seasonal variation in pCO_2 and temperature in the surface sea water. pCO_2 was measured on January 19, 1985 (+, Ry8501), February 22, 1984 (△, KH8304) and June 29, 1985 (○, KH8503).

Table 3. *Seasonal variation in the pCO_2 in the surface sea water*

Cruise	pCO_2 (ppm)	No.	T (°C)	No.	Latitude	Date
Ry8501 (1)	285.7 ± 1.9	23	19.9 ± 0.3	23	29°N–32°N	Jan. 19, 1985
KH8304	292.2 ± 2.2	14	18.9 ± 0.3	14	29°N–32°N	Feb. 22, 1984
KH8503	332.0 ± 1.2	9	24.5 ± 0.8	9	30°N–32°N	June 29, 1985

The average values of pCO_2 and water temperature in Fig. 6 are summarized in Table 3. The apparent temperature dependence of pCO_2 is calcualted at $2.7\%°C^{-1}$ at $pCO_2 = 300$ ppm. This pCO_2–T relationship is different from the relationship given by eq. (1). In this connection, Takahashi et al. (1983) have reported the apparent temperature dependence ranged from $1.2\%°C^{-1}$ to $4.7\%°C^{-1}$ in the Sargasso gyre, the Antilles current and the North Atlantic. The causes of these differences are matters for further study.

3.3. Long-term trend of pCO_2 in surface sea water

As seen in Fig. 7, the pCO_2 in the air was high near the Japanese islands and fairly constant south of 15°N. During these five years, the linear regression analysis of the data south of 15°N has shown a 1.14 ± 0.06 ppm yr^{-1} increase in atmospheric CO_2 concentration (Table 4) and it is interesting to examine whether this increase is reflected in the pCO_2 in the surface sea water in the western North Pacific. The increase in pCO_2 due to the absorption of CO_2 from air to sea water can be correlated with the incremental

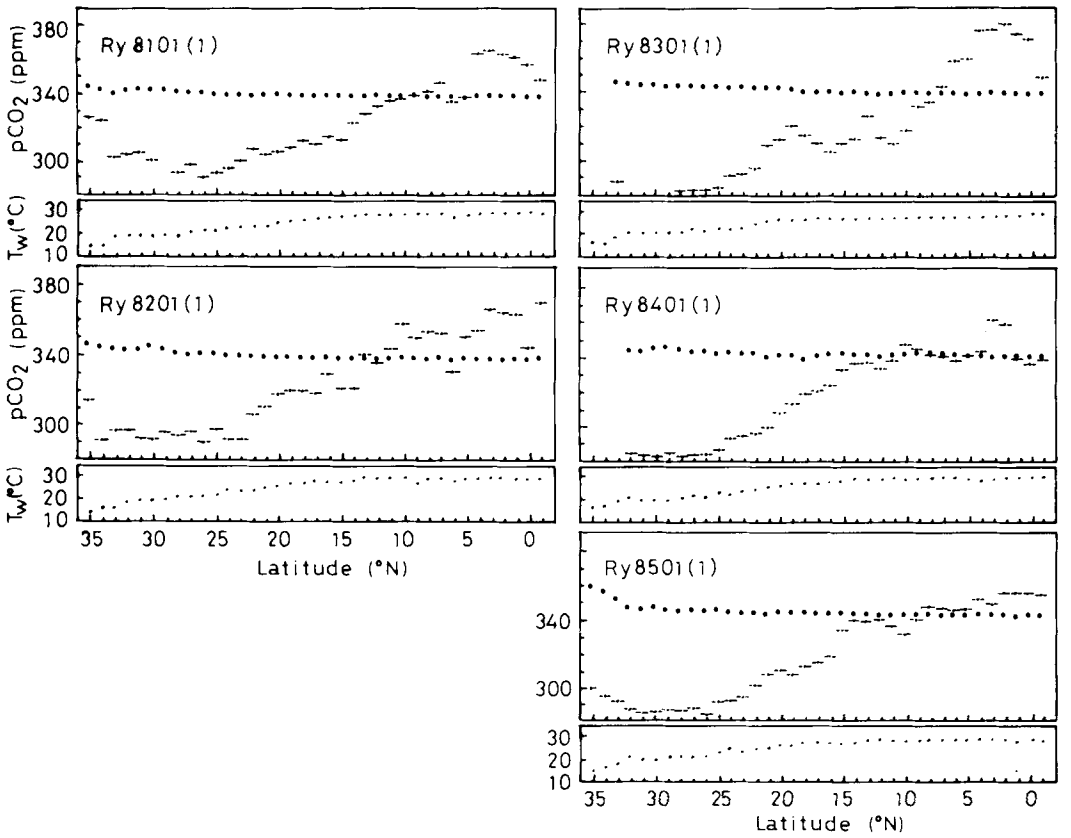

Fig. 7. Meridional distribution of the mean values of pCO_2 in the air (O) and in the surface sea water (—·—) and temperature in winter along 137°E for 1981 to 1985.

change in $\sum CO_2$ via the buffer factor of sea water (Sundquist et al., 1979; Takahashi et al., 1980). The subtropical gyre in the midlatitudes of the western North Pacific is considered to be a suitable area for the observation of secular changes in pCO_2 values in sea water. As seen in Table 1, the lowest pCO_2 values with relatively small standard deviation are seen in the area of 25°N and 26°N. These have been selected for examination, but as is also seen in the Table, the five year record does not give any clear evidence of an increase in pCO_2 in the surface sea water.

The values of the difference in the pCO_2 between air and sea water obtained 16 years ago (Miyake et al., 1974; Akiyama, 1968) agree fairly closely with those of this study. For this reason, the increase in pCO_2 is estimated to be a 10 to 20 ppm in the surface sea water for the period from 1969 to 1985. In this connection, Roos and Gravenhorst (1984) have also reported a general increase of pCO_2 in the surface sea water at about 1 ppm yr^{-1} in the North Atlantic, based on the data obtained by various methods during the last seven decades. To detect the long-term variation in pCO_2 in the surface sea water, it requires precise and continuous measurement over several years.

3.4. $\delta^{13}C$ in CO_2 of the air and in total CO_2 of surface sea water

The results of measurement of the $\delta^{13}C$ in air CO_2 over the ocean and in $\sum CO_2$ in the surface water in the western North Pacific are summarized in Table 4. The meridional distribution of the $\delta^{13}C$ is shown in Fig. 8. In the same figure, the $\delta^{13}C$ value in the air over the ocean under conditions of isotopic equilibrium is also given, based on the equilibrium fractionation factor of

Table 4. *$\delta^{13}C$ of atmospheric CO_2 and $\sum CO_2$ in the surface sea water along 137° E*

Atmospheric CO_2

Ry8101 (1)	Ry8201 (1)				Ry8301 (1)				Ry8401 (1)	Ry8501 (1)			
	Date	Latitude	pCO_2 (ppm)	δC (‰)	Date	Latitude	pCO_2 (ppm)	δC (‰)		Date	Latitude	pCO_2 (ppm)	δC (‰)
	Jan. 20	34°00′N	345.8	−8.21	Jan. 19	33°27′N	346.3	−8.26		Jan. 19	33°59′N	353.4	−8.41
	Jan. 21	30°30′	343.6	−8.10	Jan. 20	29°59′	343.8	−8.17		Jan. 20	29°11′	348.7	−8.25
	Jan. 24	22°27′	340.3	−8.03	Jan. 23	23°31′	343.4	−8.14		Jan. 21	27°00′	347.2	−7.93
	Jan. 25	18°50′	340.2	−7.63	Jan. 24	17°55′	342.0	−8.07		Jan. 22	24°14′	346.7	−8.05
	Jan. 27	10°30′	340.2	−7.97	Jan. 25	13°10′	342.1	−8.00		Jan. 23	22°07′	345.6	−8.05
	Jan. 28	7°35′	340.7	−8.03	Jan. 26	9°32′	342.0	−7.88		Jan. 24	18°04′	344.9	−8.08
	Jan. 29	5°00′	340.5	−7.99	Jan. 27	6°39′	340.7	−7.97		Jan. 25	14°59′	345.2	−8.00
	Jan. 30	3°04′	340.1	−7.75	Jan. 28	4°30′	341.6	−7.86		Jan. 26	12°05′	343.5	−7.90
	Jan. 31	0°28′	340.7	−7.57	Jan. 29	2°24′	341.4	−7.80		Jan. 26	10°02′	343.3	−7.94
	Feb. 1	0°52′S	341.0	−7.83	Jan. 30	0°29′	340.9	−8.07		Jan. 27	7°06′	343.4	−7.92
					Jan. 31	0°33′S	341.9	−7.72		Jan. 28	5°02′	344.1	−7.97
										Jan. 31	0°56′	343.5	−7.92
										Feb. 1	0°53′S	343.6	−7.84
Average (15°N-1°S)			340.5	−7.86			341.5	−7.90				343.8	−7.93
1 σ			0.3	0.18			0.5	0.12				0.7	0.05
No.			6	6			7	7				8	8

Average of each latitudinal pCO_2 (15°N-1°S)

	339.2		340.0				341.1		342.6			343.6	
1 σ	0.4		0.3				0.2		0.9			0.4	
No.	17		17				17		17			17	

$\sum CO_2$ in the surface sea water

	Ry8201 (1)				Ry8301 (1)				Ry8501 (1)			
	Date	Latitude	δC (‰)	δC_{eq} (‰)	Date	Latitude	δC (‰)	δC_{eq} (‰)	Date	Latitude	δC (‰)	δC_{eq} (‰)
	Jan. 20	34°00′N	1.13	−7.36	Jan. 19	33°58′N	0.93	−7.52	Jan. 19	33°59′N	1.05	−7.57
	Jan. 21	30°00′	1.34	−6.89	Jan. 20	30°59′	1.83	−6.27	Jan. 20	31°02′	1.84	−6.43
	Jan. 22	26°00′	1.26	−6.76	Jan. 21	28°01′	1.20	−6.71	Jan. 21	27°00′	1.52	−6.66
	Jan. 24	22°02′	1.39	−6.39	Jan. 22	24°00′	1.39	−6.49	Jan. 22	25°00′	1.07	−6.41
	Jan. 25	17°58′	1.55	−5.97	Jan. 23	20°00′	1.65	−5.80	Jan. 23	22°03′	0.91	−6.85
	Jan. 26	14°58′	0.93	−6.42	Jan. 24	17°00′	1.68	−5.78	Jan. 24	20°01′	1.07	−6.52
	Jan. 28	7°00′	1.49	−5.72	Jan. 25	14°00′	1.15	−6.30	Jan. 24	17°58′	0.72	−6.68
	Jan. 29	4°31′	1.09	−6.17	Jan. 25	13°06′	1.58	−5.80	Jan. 25	15°00′	1.42	−6.02
	Jan. 30	2°31′	1.86	−5.33	Jan. 26	10°00′	1.12	−6.28	Jan. 26	12°00′	1.32	−6.06
	Jan. 31	0°01′	1.37	−5.89	Jan. 27	7°00′	1.44	−5.90	Jan. 26	10°00′	1.03	−6.38
					Jan. 28	5°01′	1.97	−5.35	Jan. 28	7°00′	0.76	−6.63
					Jan. 29	2°30′	1.58	−5.70	Jan. 28	5°02′	1.31	−6.05
					Jan. 30	0°02′	1.60	−5.60	Jan. 28	4°57′	1.40	−5.96
									Jan. 30	3°00′	1.02	−6.25
									Jan. 31	0°02′S	1.45	−5.91
Average (35°N-1°S)			1.34				1.47				1.19	
1 σ			0.26				0.30				0.31	
No.			10				13				15	

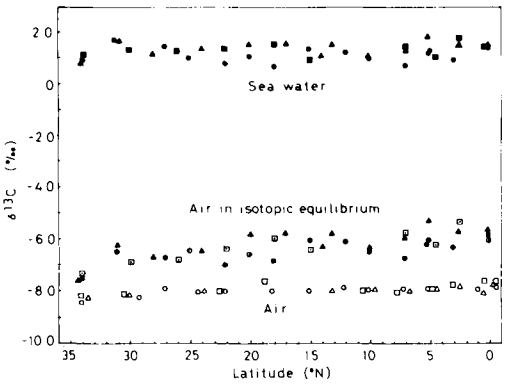

Fig. 8. Distribution of $\delta^{13}C$ of CO_2 in the air and of $\sum CO_2$ in the surface sea water along 137°E. ■, $\delta^{13}C$ of CO_2; □, $\delta^{13}C$ of air CO_2 (Ry8201). ▲, $\delta^{13}C$ of CO_2; △, $\delta^{13}C$ of air CO_2 (Ry8301). ●, $\delta^{13}C$ of CO_2; ○, $\delta^{13}C$ of air CO_2 (Ry8501). ⊡, $\delta^{13}C$ of air CO_2 in isotopic equilibrium (Ry8201). ⧋, $\delta^{13}C$ of air CO_2 in isotopic equilibrium (Ry8301). ⊙, $\delta^{13}C$ of air CO_2 in isotopic equilibrium (Ry8501).

carbon isotopes between air and sea water (Kroopnick, 1974; Inoue and Sugimura, 1985a). The isotopic ratio of $\sum CO_2$ in the surface water ranged from 0.7‰ to 2.0‰ and that of the air CO_2 was about −8‰ as seen in Table 4 and Fig. 8. The observed $\delta^{13}C$ value of the air CO_2 deviates negatively from the equilibrium value from 1 to 3‰. The relationship between concentration and $\delta^{13}C$ of atmospheric CO_2 is shown in Fig. 9. For presentation of the data, the linear long-term trend of CO_2 increase and $\delta^{13}C$ decrease was removed in advance. The result

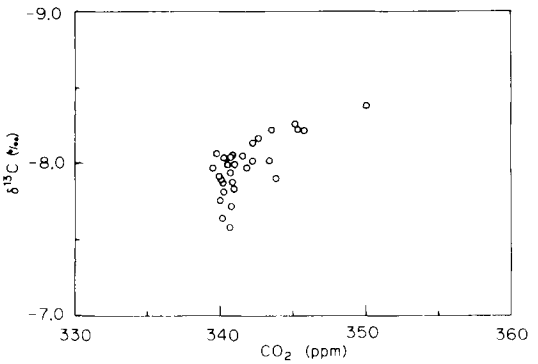

Fig. 9. Relationship between $\delta^{13}C$ and pCO_2 with the linear time trend removed. Samples were collected from 35°N to 1°S along 137°E in 1982, 1983 and 1985.

indicates that $\delta^{13}C$ in the air CO_2 decreases with the concentration rise as seen in the land air.

The sample air collected off Japan southwards to 30°N showed relatively high concentration and a low $\delta^{13}C$ value of the air CO_2. The carbon isotopic ratio of CO_2 added to the background air CO_2 is estimated to be -27.5 ± 3.4‰, $r = 0.72$ and $n = 32$ by using the single mixing equation (Keeling, 1958, 1961). This agrees with the value of biospheric or fossil fuel origin. Therefore, the decrease in the CO_2 concentration in the air over the ocean with distance from the Japanese islands was found to be caused by the simple mixing between air from the land and air from over the ocean.

3.5. Detection of long-term trend of $\delta^{13}C$ change

It is of interest to see the variation of the $\delta^{13}C$ value as it corresponds to the variation of CO_2 concentration in maritime air. Because the sampling of the air was performed at the same season every year, seasonal correction was ignored in this examination. As mentioned above, the concentration of CO_2 in the air over the area from 15°N to the equator shows a fairly constant distribution (Fig. 7). Therefore, this area was selected for the examination of the secular trend of maritime air CO_2.

The mean values of the concentration and $\delta^{13}C$ of the air CO_2 are shown in Table 4. The lienar regression analysis gives a 1.11 ± 0.04 ppm yr^{-1} increase in the concentration and a 0.022 ± 0.006‰ yr^{-1} decrease in the $\delta^{13}C$ during these four years. Similar results are given by Keeling et al. (1979, 1984) and Mook et al. (1983).

For the long-term linear trend, a change in the $\delta^{13}C$ per ppm increase in the CO_2 concentration is about half that of diurnal and seasonal variation due to fossil-fuel combustion or air/biosphere CO_2 exchange. The observed data clearly indicates the influence of air/sea CO_2 exchange on the relationship between concentration and $\delta^{13}C$ of atmospheric CO_2. The exchange of atmospheric CO_2 with the biospheric carbon gives around −25‰ as the $\delta^{13}C$ value of CO_2 added to or extracted from the air (Keeling, 1958, 1961). The carbon isotopic ratio of CO_2 passed through the air/sea interface is estimated to be about −10‰ for air to sea and −8‰ for sea to air, when CO_2 exchange takes place between

air (−8‰) and surface sea water (+2‰) at 15°C (Inoue and Sugimura, 1985a).

With the changing $\delta^{13}C$ of atmospheric CO_2, $\delta^{13}C$ of $\sum CO_2$ in sea water should change gradually, but no observable change is given as yet for the long-term trend in $\delta^{13}C$ of $\sum CO_2$ in sea water due to the absorption of anthropogenic CO_2 from the air, although Kroopnick (1985) has calculated the $\delta^{13}C$ decrease by 0.5‰ from the preindustrial value of approximately 2.5‰. During these four years, the $\delta^{13}C$ value of $\sum CO_2$ in the surface sea water did not vary significantly from an average value of 1.33 ± 0.31‰ ($n = 31$). The presence of a huge amount of inorganic carbon in sea water and relatively powerful effects of oceanographic conditions on $\delta^{13}C$ made it difficult to detect a slight long-term variation within just a few years. In order to achieve further understanding of the role of air/sea CO_2 exchange and carbon transfer from mixed layer to deep sea in the global carbon budget, the long-term variation in $\delta^{13}C$ of $\sum CO_2$ in sea water should be characterized by a study lasting at least a few decades as Mauna Loa's observation. It will be possible to estimate the relative contributions of air/sea and air/biosphere CO_2 exchange by continuous study, both of the long-term trend of $\delta^{13}C$ and of the difference in pCO_2 between air and surface sea water.

4. Summary

To clarify the air/sea CO_2 exchange based on the secular trend of pCO_2 and $\delta^{13}C$ of CO_2 in the air and surface sea water, measurement of pCO_2 and $\delta^{13}C$ of CO_2 was carried out in winter in and over the western North Pacific over a period from 1981 to 1985. A study of the seasonality of pCO_2 in the surface sea water was also conducted in the area off the coast of Japan. The partial pressure of CO_2 in the surface sea water is high in the coastal area off Japan and in the equatorial region, and low in the subtropical gyre. The highest value of pCO_2 in the surface sea water appeared in the south equatorial current (2°N to 4°N) and ranged from 356.6 ppm to 390.7 ppm, while the lowest was found ranging from 282.5 ppm to 290.7 ppm in the temperate zone (26°N to 31°N). The El Niño Event in 1982/83 significantly modified the distribution of temperature and pCO_2 in the waters south of 17°N in the western North Pacific; pCO_2 in the area from 7°N to 1°S along 137°E and from 1°S, 137°E to 15°N 131°30′E increased with the temperature decrease, and pCO_2 in the waters of the north equatorial current from 17°N to 7°N along 137°E decreased with the temperature decrease.

The surface sea water in the area off Japan's coast shows a broad seasonal variation in pCO_2, which is low in winter (285.7 ppm, 19.7°C) and high (332.0 ppm, 24.5°C) in summer. The annual cycle of pCO_2 in the surface sea water significantly affects the exchange between air and sea water.

The concentration of CO_2 in the air over the ocean decreased with distance from the Japanese islands, and south of 15°N it was nearly constant. The magnitude of $\delta^{13}C$ of atmospheric CO_2 showed a similar distribution. The carbon isotopic ratio of CO_2 added to the air over the Japanese islands is estimated to be −27.5‰, which indicates the CO_2 released from respiration by land plants and soils or from fossil fuel combustion. From 1982 to 1985 the concentration of CO_2 in the air has increased at 1.11 ± 0.04 ppm yr^{-1} and the $\delta^{13}C$ of atmospheric CO_2 has decreased at 0.022 ± 0.006‰ yr^{-1}. This indicates the influence of air/sea CO_2 exchange on the long-term trend, and will be studied further in order to distinguish between air/sea and air-biosphere CO_2 exchange.

The long-term trend of pCO_2 and $\delta^{13}C$ in the surface sea water as a result of air/sea CO_2 exchange and carbon transfer from mixed layer to deep sea, was not clear from these observations from 1981 to 1985, although a comparison with data of decades ago suggests slow changes in the pCO_2 and $\delta^{13}C$ of the carbonate system in the sea water.

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