**Shipboard measurements of atmospheric and surface seawater $p\text{CO}_2$
in the North Pacific carried out from January 1999 to October 2000
on the voluntary observation ship MS *Alligator Liberty***

by

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Abstract

Partial pressures of CO_2 in surface seawater ($p\text{CO}_2^{\text{sea}}$) and the overlying air ($p\text{CO}_2^{\text{air}}$) were measured in the North Pacific (mainly 30–40°N) from January 1999 to October 2000 (9 cruises) onboard the voluntary observation ship MS *Alligator Liberty*. Distributions of $p\text{CO}_2^{\text{air}}$ and $p\text{CO}_2^{\text{sea}}$ showed that the western North Pacific (west of 180°) acted as a sink for atmospheric CO_2 throughout the year except for August, whereas the eastern North Pacific (east of 160°W) acted as a sink for only half the year (November to May). Total dissolved inorganic carbon (TCO_2) estimated from $p\text{CO}_2^{\text{sea}}$ and total alkalinity showed a larger seasonal decrease (April to June) in the western North Pacific than in the eastern North Pacific, in accordance with the seasonal decrease in nitrate + nitrite ($\text{NO}_x = \text{NO}_3^- + \text{NO}_2^-$). The 9.5 C/N ratio calculated from the relationship between decreased TCO_2 and $[\text{NO}_x]$ implied a larger influence of biological activity in the western North Pacific. Using $p\text{CO}_2^{\text{sea}}$ estimated from the relationship between $p\text{CO}_2^{\text{sea}}$ and sea surface temperature, we assessed the monthly CO_2 fluxes in the western North Pacific for the year 2000. The fluxes ranged from ca. 0 Gt-C yr^{-1} in the summer to ca. -0.4 Gt-C yr^{-1} in the winter, with an annual average of -0.2 Gt-C yr^{-1} , which corresponds to about 10% of the annual oceanic CO_2 uptake over the 1990s.

1. Introduction

The ocean plays an important role in determining the level of atmospheric CO_2 , which has been increasing due to human activities. The current estimation of the distribution of CO_2 among carbon reservoirs, however, remains uncertain (IPCC, 1995, 2001). Measurements of the partial pressures of CO_2 in the ocean surface ($p\text{CO}_2^{\text{sea}}$) and the

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overlying air ($p\text{CO}_2^{\text{air}}$) are important to estimate the oceanic CO_2 uptake, because the fluxes of CO_2 across the air–sea interface are driven by differences of $p\text{CO}_2$ between the two phases.

According to Takahashi *et al.* (2002), approximately 940,000 measurements of $p\text{CO}_2^{\text{sea}}$ of the global ocean have been made since the International Geophysical Year of 1957–1958. Because of the paucity of $p\text{CO}_2^{\text{sea}}$ data collected during this period, they estimated CO_2 fluxes between the sea and air for the single virtual calendar year of 1995 by compiling data collected over 40 years. Their results indicated that there were insufficient $p\text{CO}_2^{\text{sea}}$ data to elucidate interannual to decadal variations in CO_2 fluxes between the sea and air, which are the characteristic timescales necessary to understand the current global carbon cycle (IPCC, 1995).

Due to technical issues that remain to be solved, platforms for measurement of $p\text{CO}_2^{\text{sea}}$ have long been limited to research vessels. However, measurement of $p\text{CO}_2^{\text{sea}}$ by automated systems onboard voluntary observation ships is now recognized to be a useful way to investigate variations of the oceanic carbonate system. Recently, extensive development of a CO_2 measuring system has made it possible to utilize commercial “vessels of opportunity” for $p\text{CO}_2$ measurements along their regular trade routes. Cooper *et al.* (1998) reported an annual variation of $p\text{CO}_2^{\text{sea}}$ in the North Atlantic, using an onboard unattended measurement system. Lefèvre *et al.* (1999) assessed the seasonality of the oceanic sink for CO_2 in the Northern Hemisphere, using data collected on the M/V *Prince of Seas* between the UK and Costa Rica, and the RMS *St. Helena* between the UK and South Africa. Lüger *et al.* (2004) reported results of 1 year of automated $p\text{CO}_2^{\text{sea}}$ measurements made onboard the car carrier M/V *Falstaff* during 2002–2003 and analyzed factors controlling $p\text{CO}_2^{\text{sea}}$ in the midlatitude North Atlantic Ocean.

In a study of the CO_2 flux in the Pacific, Inoue and

Sugimura (1992) combined $p\text{CO}_2^{\text{sea}}$ data collected over the period from 1987 to 1989 aboard research and commercial vessels (MS *Wellington-maru* and MS *Yashirogawa-maru*) and reported variations in CO_2 outflux in the equatorial Pacific. Wong *et al.* (1993) also reported the CO_2 fluxes in the equatorial Pacific during 1986–1987 El Niño, utilizing data collected onboard the MS *Lillooet* between Canada and Australia. They also investigated geographical, seasonal, and interannual variations of air–sea CO_2 exchange in subtropical Pacific surface water during 1983–1988 (Wong *et al.*, 1995a, 1995b). Zeng *et al.* (2002) constructed monthly distributions of $\Delta p\text{CO}_2$ in the northern North Pacific based on measurements made onboard the commercial vessel M/S *Skaugran* in 1995–1999 and reported a small sink ($-0.26 \text{ Gt-C yr}^{-1}$) for atmospheric CO_2 . Despite these extensive efforts, vast areas still lack $p\text{CO}_2^{\text{sea}}$ data. In particular, the transitional area between the subtropical and subarctic gyres in the North Pacific needs to be surveyed intensively, because the area is one of the largest sinks in the global oceans (Takahashi *et al.*, 2002).

The objective of the present study was to examine temporal and spatial distributions of $p\text{CO}_2^{\text{sea}}$ in the North Pacific, especially in the transitional area between the subtropical and subarctic gyres. For this purpose, we installed an underway $p\text{CO}_2$ measuring system onboard the container ship MS *Alligator Liberty* (Mitsui O.S.K. Lines, Ltd.).

The outline of our paper is as follows. In Section 2, we describe the shipboard measurements of $p\text{CO}_2^{\text{air}}$ and $p\text{CO}_2^{\text{sea}}$ carried out on the voluntary observation ship. In Section 3, we discuss the distributions of $p\text{CO}_2^{\text{air}}$ and $p\text{CO}_2^{\text{sea}}$ along the cruise routes, with special reference to oceanic sinks and sources for atmospheric CO_2 . In Section 4, we estimate the air–sea fluxes of CO_2 and evaluate the CO_2 sink capacity in the area. We conclude with a short summary and some closing remarks.

Fig. 1 Cruise tracks of the MS *Alligator Liberty* between Tokyo, Japan, and Manzanillo, Republic of Panama, from January 1999 to October 2000: thin dotted lines, winter cruise (from December to February); thick dotted line, spring cruise (from March to May); solid line, summer cruise (from June to August); dash-dotted line, fall cruise (from September to November). The cruise track for June 2000 (not shown) was almost same as that for April 2000.

Table 1 Cruise information

Cruise date	Cruise name	Northernmost position
January 23–February 10, 1999	080E	36°N, 158°E
May 29–June 15, 1999	082E	44°N, 170°W
August 1–17, 1999	083E	44°N, 174°W
December 4–21, 1999	085E	36°N, 172°E
February 6–23, 2000	086E	34°N, 141°E
April 8–26, 2000	087E	40°N, 175°E
June 10–27, 2000	088E	40°N, 178°E
August 13–29, 2000	089E	45°N, 176°W
October 14–31, 2000	090E	39°N, 170°E

2. Shipboard measurements

Measurements of pCO₂^{sea} and pCO₂^{air} were made in the North Pacific (Tokyo, Japan to Manzanillo, Republic of Panama) onboard the voluntary observation ship MS *Alligator Liberty* (Mitsui O.S.K. Lines, Ltd.) during 9 cruises from January 1999 to October 2000 (Table 1, Fig. 1). We operated our underway pCO₂ measuring system on the eastbound cruises.

All the data for pCO₂^{sea}, pCO₂^{air}, temperature, and salinity reported here are available from the World Meteorological Organization/World Data Centre for Greenhouse Gases (WMO/WDCGG), Japan Meteorological Agency (JMA), Tokyo Japan.

2.1. Onboard pCO₂ measuring system

We installed our system for measuring pCO₂^{sea} and pCO₂^{air} in the air-conditioned control room of the MS *Alligator Liberty*. The system also monitored sea surface temperature (SST), sea surface salinity (SSS), flow rate of seawater, and seawater level in an equilibrator. The details of the system are reported elsewhere (Foundation for Promoting Personal Mobility and Ecological Transportation, 2001).

The system is basically the same as that reported previously (Hirota *et al.*, 1991; Inoue *et al.*, 1999; Körtzinger *et al.*, 2000). It consists of a nondispersive infrared gas analyzer (BINOS, MLT 3.1, Fisher-Rosemount GmbH & Co.), two electric dehumidifiers, a Nafion tube (Perma Pure Inc.), a chemical desiccant column (Mg(ClO₄)₂), a shower-head-type water–gas equilibrator, diaphragm pumps, a series of solenoid valves, and a data acquisition unit connected to a personal computer. Water temperature in the equilibrator was measured with a Pt 100-ohm thermometer. The CO₂ measuring system was calibrated onboard with 4 reference gases (nominally 272, 330, 360, 405 ppm), which were calibrated before and after the cruise against standard JMA gases, traceable to the WMO mole fraction scale (Watanabe *et al.*, 2000).

2.2. Sea surface temperature (SST) and salinity (SSS)

To measure the SST, we placed a flat-head-type thermocouple probe on the sea chest (very close to the water inlet, ~11 m below the sea surface). The SST was monitored every 5 min. SSS was measured by introducing seawater into a container (20 L) and immersing CTD sensors (SBE21, Sea Bird Co. Ltd.) into it.

Surface seawater was sampled twice a day from the upper deck using a Kamiya-type sampler for measurements of temperature and salinity. We confirmed that the water temperature at the sea chest coincided with that in the sampler within ±0.1 °C and that the salinity measured by the CTD sensor usually coincided within ±0.005 with laboratory measurements on land.

Water temperature typically increased by 0.3 °C from the seawater inlet to the equilibrator. To correct pCO₂^{sea} for increasing water temperature, we used the equation given by Gordon and Jones (1973).

2.3. Sea surface nutrients

During the cruise in August 1999, surface seawater samples for nutrient determination were collected in 10-mL screw-capped test tubes 2 or 4 times a day from a tap attached to the seawater line of the CO₂ measuring system. The samples were frozen and stored until laboratory analysis on land. The concentrations of nitrate + nitrite (hereafter denoted NO_x) and phosphate (PO₄) in seawater were determined by the method of Strickland and Parsons (1972) using an autoanalyzer (AACS III, Bran+Luebbe, Germany).

3. Results and discussion

Figure 1 shows the tracks of the 9 cruises from January 1999 to October 2000 (Table 1), when the pCO₂ measurements were made. Since the season and route varied from cruise to cruise, characterizing the temporal and spatial variations of pCO₂^{air} and pCO₂^{sea} was difficult. To outline the tendencies of the distributions of pCO₂^{air} and pCO₂^{sea}, we first analyze our data by summarizing a few months (seasonal) of data at a time, neglecting year-to-year differences (Section 3.1). Then, using selected data, we examine seasonal variations of pCO₂^{sea} (Section 3.2).

3.1. General views of the pCO₂^{air} and pCO₂^{sea} distributions

3.1.1. January–February (080E and 086E cruises)

pCO₂^{air} was almost constant along the cruise track, and was generally higher than pCO₂^{sea} (Fig. 2a). West of 150°W, pCO₂^{sea} was almost constant (310 ± 10 μatm), whereas east of 150°W, pCO₂^{sea} increased gradually to the east. As a whole, distributions of pCO₂^{sea} as a function of longitude showed gradual variations. This is probably because, on these cruises, the ship sailed mostly in the subtropical gyre

south of 36°N, where nutrients are almost depleted (Fig. 2b) and variation of $p\text{CO}_2^{\text{sea}}$ is mostly controlled by variations of SST and SSS (Inoue *et al.*, 1995, 2003). In this season, the area overall acted as a sink for atmospheric CO_2 .

3.1.2. April–June (082E, 087E, and 088E cruises)

The $p\text{CO}_2^{\text{air}}$ in this season was highest (~ 370 μatm ; Fig. 3a) among all data collected during the 9 cruises. The high $p\text{CO}_2^{\text{air}}$ was mainly caused by the seasonal increase in atmospheric CO_2 concentration from winter to spring in the Northern Hemisphere (Conway *et al.*, 1994).

Spatial variations of $p\text{CO}_2^{\text{sea}}$ in this season were larger than those in Fig. 2, and this difference is attributable to northward shifts of the cruise tracks (up to 40–44°N; Table 1, Fig. 1). That is, the ship entered the transitional area between the subtropical and subarctic gyres, where $p\text{CO}_2^{\text{sea}}$ is usually affected not only by SST and SSS but also by biological activity (Takahashi *et al.*, 2002). Consequently, the $p\text{CO}_2^{\text{sea}}$ –SST relationship became complicated, and

$p\text{CO}_2^{\text{sea}}$ showed variations associated with those of NO_x and PO_4 (Fig. 3b). For example, from 140 to 160°E, $p\text{CO}_2^{\text{sea}}$ increased as SST decreased on the 087E cruise (April 2000), whereas $p\text{CO}_2^{\text{sea}}$ decreased as SST decreased on the 082E cruise (late May–June 1999) and the 088E cruise (June 2000); in April 2000, $p\text{CO}_2^{\text{sea}}$ decreased as SST increased from 160°E to 150°W, whereas $p\text{CO}_2^{\text{sea}}$ increased as SST increased east of 150°W. A positive correlation between $p\text{CO}_2^{\text{sea}}$ and SST (subtropical characteristics; 140 to 160°E in late May–June 1999 and June 2000, east of 150°W in June 2000) was observed in the area with depleted nutrients, indicating relatively large effects of thermodynamics. On the other hand, a negative $p\text{CO}_2^{\text{sea}}$ –SST relationship (subarctic characteristics; 140 to 160°E in April 2000, 160°E to 150°W in June 2000) was found in the area with relatively rich nutrients, indicating relatively large effects of the entrainment of total inorganic carbon (TCO_2) from the lower layer. In late May–June 1999, $p\text{CO}_2^{\text{sea}}$ varied steeply around 160°W, but both SST and SSS varied monotonously

Fig. 2 Longitudinal distributions of surface properties observed in January–February 1999 (080E) and February 2000 (086E). (a) $p\text{CO}_2^{\text{air}}$ (open circle, January–February 1999; plus, February 2000) and $p\text{CO}_2^{\text{sea}}$ (dashed line, January–February 1999; solid line, February 2000). (b) NO_x (open circle) and PO_4 (open triangle) in February 2000. (c, d) SSS and SST (dashed line, January–February 1999; solid line, February 2000).

Fig. 3 Longitudinal distributions of surface properties observed in May–June 1999 (082E), April 2000 (087E), and June 2000 (088E). (a) $p\text{CO}_2^{\text{air}}$ (open circle, May–June 1999; plus, April 2000; open triangle, June 2000) and $p\text{CO}_2^{\text{sea}}$ (thin solid line, May–June 1999; thick dashed line, April 2000; thick solid line, June 2000). (b) NO_x (open circle, April 2000; solid circle, June 2000) and PO_4 (open triangle, April 2000; solid triangle, June 2000). (c, d) SSS and SST (thin solid line, May–June 1999; thick dashed line, April 2000; thick solid line, June 2000).

(nutrients were not measured on this cruise). In the same area, no clear steep variations of $p\text{CO}_2^{\text{sea}}$ occurred in June 2000.

In this season, $p\text{CO}_2^{\text{sea}}$ showed an overall increase from west to east. Consequently, the area west of 150°W acted as a sink for atmospheric CO_2 , whereas the area east of 150°W generally acted as a source of atmospheric CO_2 .

3.1.3. August (083E and 089E cruises)

During these cruises, the ship took a northern route up to $44\text{--}45^\circ\text{N}$ ($180\text{--}170^\circ\text{W}$) and then headed southward down to 29°N , 120°W (Fig. 1). $p\text{CO}_2^{\text{air}}$ exhibited a greater variation in this season (Fig. 4a) than in other seasons, probably due to differences in air masses.

Spatial variations of $p\text{CO}_2^{\text{sea}}$ in August (Fig. 4a) were as large as those in the April–June season (Fig. 3a); in August 1999, $p\text{CO}_2^{\text{sea}}$ varied steeply from 400 to $320\text{ }\mu\text{atm}$ around 160°W , but with monotonous variations of SST and SSS (Figs. 4c and 4d). At 158°E , 161°E , and 170°E , $p\text{CO}_2^{\text{sea}}$

showed large variations, but SST and SSS exhibited no such variations. Between 150 and 170°W and east of 130°W , $p\text{CO}_2^{\text{sea}}$ in August 2000 showed distributions greatly different from those in August 1999. In particular, no steep variation of $p\text{CO}_2^{\text{sea}}$ occurred around 160°W in August 2000.

The concentrations of nitrate and phosphate were low in both the western and eastern subtropical North Pacific (Fig. 4b). On the other hand, significant increases in both concentrations were observed in the transitional area around $160^\circ\text{E}\text{--}160^\circ\text{W}$ (highest concentrations: $11.8\text{ }\mu\text{mol/kg}$ for nitrate and $1.15\text{ }\mu\text{mol/kg}$ for phosphate). Corresponding to the above-mentioned steep decrease in $p\text{CO}_2^{\text{sea}}$ of $\sim 50\text{ }\mu\text{atm}$ around 160°W (43°E) in August 1999, nutrient concentrations decreased significantly from 163°W to 155°W . From the combination of the decrease in nitrate of $6\text{ }\mu\text{mol/kg}$ and a C/N ratio of 9.5 for biological consumption (cf. Section 3.2), we expected a TCO_2 change of $-57\text{ }\mu\text{mol/kg}$ and subsequent $p\text{CO}_2^{\text{sea}}$ change of $-90\text{ }\mu\text{atm}$.

Fig. 4 Longitudinal distributions of surface properties observed in August 1999 (083E) and August 2000 (089E). (a) $p\text{CO}_2^{\text{air}}$ (open circle, August 1999; plus, August 2000) and $p\text{CO}_2^{\text{sea}}$ (dashed line, August 1999; solid line, August 2000). (b) NO_x (open circle, August 1999; solid circle, August 2000) and PO_4 (open triangle, August 1999; solid triangle, August 2000). (c, d) SSS and SST (dashed line, August 1999; solid line, August 2000).

Fig. 5 Longitudinal distributions of surface properties observed in December 1999 (085E) and October 2000 (090E). (a) $p\text{CO}_2^{\text{air}}$ (open circle, December 1999; plus, October 2000) and $p\text{CO}_2^{\text{sea}}$ (dashed line, December 1999; solid line, October 2000). (b) NO_x (open circle, December 1999; solid circle, October 2000) and PO_4 (open triangle, December 1999; solid triangle, October 2000). (c, d) SSS and SST (dashed line, December 1999; solid line, October 2000).

Considering that an SST increase of 1.5 °C leads to a $p\text{CO}_2^{\text{sea}}$ change of +20 μatm , we calculated a total $p\text{CO}_2^{\text{sea}}$ drawdown of $-70 \mu\text{atm}$. Taking into account the scattering of the C/N ratio for biological consumption (shown in Fig. 6), a major portion of the $p\text{CO}_2^{\text{sea}}$ drawdown — $\sim 50 \mu\text{atm}$ around 160°W — could be explained by biological consumption.

$p\text{CO}_2^{\text{sea}}$ was generally higher than $p\text{CO}_2^{\text{air}}$, meaning that in this season, the area generally acted as a source for atmospheric CO_2 .

3.1.4. October and December (085E and 090E cruises)

The distributions of $p\text{CO}_2^{\text{sea}}$ (Fig. 5a) in October and December, like those in the January–February season, showed a small variation (Fig. 2a). This is probably because the ship took a southern route, entering the subtropical gyre with low concentrations of nitrate ($<1.1 \mu\text{mol/kg}$) and phosphate ($<0.19 \mu\text{mol/kg}$) (Fig. 2b), and because the seasons were alike.

The decrease in $p\text{CO}_2^{\text{sea}}$ of 30 μatm from 140°E to 180° in October 2000 was smaller than that due to the thermodynamic effect of an SST decrease of 9 °C. On the other hand, the increases in $p\text{CO}_2^{\text{sea}}$ of 70 μatm from 170 to 145°W in October 2000 and of 60 μatm from 160 to 120°W in December 1999 were larger than those due to the thermodynamic effects of SST increases of 3 and 2 °C, respectively. We believe that these variations of $p\text{CO}_2^{\text{sea}}$ are influenced by the supply of TCO_2 from the lower layer due to enhanced vertical mixing in these seasons.

In this season, the area overall acted as a sink for atmospheric CO_2 .

3.1.5. CO_2 sinks and sources

From the distributions of $p\text{CO}_2^{\text{air}}$ and $p\text{CO}_2^{\text{sea}}$ (Figs. 2a–5a), we summarize as follows: west of 180°, the area acted as a sink for atmospheric CO_2 throughout the year except for August, whereas east of 160°W, it acted as a sink for only half the year (December to May).

3.2. Seasonal variability of $p\text{CO}_2^{\text{sea}}$

Among the 9 cruises, the MS *Alligator Liberty* steamed from Tokyo to Manzanillo along the same cruise track in April 2000 and June 2000, which allows us to evaluate seasonal variations of $p\text{CO}_2^{\text{sea}}$ from April to June. We examined variations of $p\text{CO}_2^{\text{sea}}$ against those of SST, SSS, and NO_x during these two cruises.

In the eastern subtropical North Pacific, NO_x was depleted throughout the year. West of 180°, the NO_x concentrations decreased significantly from April to June, which means that biological activity has a larger effect on the surface carbonate system in the western North Pacific than in the eastern North Pacific (Takahashi *et al.*, 1993). In fact, we found that $p\text{CO}_2^{\text{sea}}$ varied according to NO_x

concentration ($>1 \mu\text{mol/kg}$). Assuming a thermodynamic temperature effect on $p\text{CO}_2^{\text{sea}}$, we calculated $p\text{CO}_2^{\text{sea}}$ normalized ($n\text{-}p\text{CO}_2^{\text{sea}}$) to the average SST temperature (13.8 °C) for the two cruises. Using the equation given by Millero *et al.* (1998), we estimated the total alkalinity in surface waters. From $n\text{-}p\text{CO}_2^{\text{sea}}$ and total alkalinity, we calculated the TCO_2 concentrations, using the chemical equilibrium constants recommended by DOE (1994).

Figure 6 illustrates the relationship between TCO_2 and NO_x concentration ($>1 \mu\text{mol/kg}$). Linear least-squares regression analysis gave 9.5 as the TCO_2 increase per unit increase of NO_x concentration, which is slightly larger than the Redfield C/N ratio (6.6). Figure 6 clearly indicates that seasonal variations of $p\text{CO}_2^{\text{sea}}$ can be well accounted for by the effects of thermodynamics and biological activity.

4. Air–sea exchanges of CO_2

4.1. Calculation of air–sea fluxes of CO_2

Air–sea fluxes of CO_2 (F_{CO_2}) were calculated as the product of the gas-transfer velocity K_{CO_2} as a function of wind speed (Wanninkhof, 1992; Wanninkhof and McGills, 1999), the solubility of CO_2 (β ; Weiss, 1974), and the partial pressure difference in $p\text{CO}_2$ between the sea surface and the air ($\Delta p\text{CO}_2$) as follows:

$$\begin{aligned} F_{\text{CO}_2} &= K_{\text{CO}_2} \times \beta \times (p\text{CO}_2^{\text{sea}} - p\text{CO}_2^{\text{air}}) \\ &= K_{\text{CO}_2} \times \beta \times \Delta p\text{CO}_2 \end{aligned} \quad (1).$$

We used Eq. (2) to compute the gas-transfer velocity from wind speed data (Wanninkhof, 1992):

$$K_{\text{CO}_2} = 0.39 w_{10}^2 (660/Sc)^{0.5} \quad (2),$$

where Sc is the Schmidt number of CO_2 at the observed SST and SSS (660 is the Schmidt number of CO_2 in seawater at 20 °C) and w_{10} is the wind speed in m s^{-1} at a height of 10 m. For the wind speed, we used the NCEP/ NCAR reanalysis data (Kalnay *et al.*, 1996). Since the NCEP/NCAR reanalysis data are prepared for a $2.5^\circ \times 2.5^\circ$ grid, the wind speed was linearly interpolated into $1^\circ \times 1^\circ$ pixels.

4.2. Interpolation/extrapolation of $p\text{CO}_2^{\text{sea}}$

Relationships between $p\text{CO}_2^{\text{sea}}$ and SST have been used extensively to estimate $p\text{CO}_2^{\text{sea}}$ distributions on a basin scale (e.g., Tans *et al.*, 1990; Ishii *et al.*, 2004). In the present study, we also attempted to use a $p\text{CO}_2^{\text{sea}}$ –SST relationship.

Using $p\text{CO}_2^{\text{sea}}$ data taken during the 9 cruises of the MS *Alligator Liberty*, we examined distributions of $p\text{CO}_2^{\text{sea}}$

Fig. 6 Relationship between calculated TCO₂ and NO_x concentration in April 2000 (solid triangle) and June 2000 (solid circle). [NO_x] data with values <1 μmol/kg were deleted from the figure. The solid line shows the relationship between TCO₂ and [NO_x]: $TCO_2 = (1986.6 \pm 5.5) + (9.521 \pm 0.855) \times [NO_x]$ ($\gamma = 0.869$, $P < 0.001$, $1\sigma = 13.7 \mu\text{mol/kg}$, $n = 42$).

Fig. 7 Temperature dependence of pCO₂^{sea} south of 40°N in the western North Pacific (a) and eastern North Pacific (180°–122°W; b). (a) Solid line shows pCO₂^{sea} calculated as a function of a second-degree polynomial of SST: $pCO_2^{sea} = (506.0 \pm 5.4) - (22.45 \pm 0.59) \times SST + (0.6349 \pm 0.0161) \times SST^2$ ($\gamma = 0.851$, $P < 0.001$, $1\sigma = 9.6 \mu\text{atm}$, $n = 611$).

as a function of SST (Fig. 7). From Fig. 7a, we found that a simple pCO₂^{sea}–SST relationship (quadratic function) existed in the western North Pacific (30–40°N, 140°E–180°) throughout the year. However, pCO₂^{sea} in the

Fig. 8 Annual mean of ΔpCO₂ (μatm) in the western part of the North Pacific (30–40°N, 140°E–180°) in 2000. Negative ΔpCO₂ means a sink for atmospheric CO₂.

Fig. 9 Annual mean of CO₂ flux between the sea and the air (moles of CO₂ m⁻² yr⁻¹) in the western part of the North Pacific (30–40°N, 140°E–180°) in 2000. A negative value means an uptake of CO₂ from the atmosphere.

latitudinal zone between 30 and 40°N of the eastern North Pacific (180° to 122°W) did not reveal a simple pattern (Fig. 7b), implying that estimation of pCO₂^{sea} distributions from the SST field is difficult in the eastern North Pacific. Therefore we decided to interpolate/extrapolate pCO₂^{sea} and to calculate ΔpCO₂ and CO₂ fluxes only in the western North Pacific covering the area from 30 to 40°N and 140°E to 180° (Fig. 1). The monthly mean SST data were taken from Reynolds and Smith (1994) (<ftp://ftp.ncep.noaa.gov/pub/cmb/sst/oimonth>).

In the western North Pacific, ΔpCO₂ is largest around the area with an SST of 16–19 °C because, under this condition, pCO₂^{sea} is lowest (Fig. 7a). In other words, for the same gas-transfer coefficient, the ocean absorbs CO₂ most efficiently in the area of this SST. The North Pacific Subtropical Mode Water (NPSTMW), characterized by an average temperature of 16.5–18.5 °C, forms and subducts through seasonal cooling at the ocean surface in the transitional area between the subtropical and subarctic gyres (Masuzawa, 1969; Taneda *et al.*, 2000). This downward movement of NPSTMW is believed to be accompanied by absorption of CO₂. Therefore, the transitional area is a typical example of this situation, and absorption of CO₂ was largest in this area.

4.3. $\Delta p\text{CO}_2$ and air–sea fluxes of CO_2 in the western North Pacific

The calculated annual mean $\Delta p\text{CO}_2$ field for the year 2000 is shown in Fig. 8. This figure indicates that the western North Pacific acted as a strong sink for atmospheric CO_2 . Large negative values of $\Delta p\text{CO}_2$ predominate in the northeastern area, which was caused by the decreases in $p\text{CO}_2^{\text{sea}}$ associated with a low SST. Small negative values of $\Delta p\text{CO}_2$ occurred in the subtropics gyre, which was caused by the increases in $p\text{CO}_2^{\text{sea}}$ in response to the warmer SST of the Kuroshio.

The annual mean of the CO_2 fluxes in 2000 is illustrated in Fig. 9. Distributions of the CO_2 fluxes revealed an east–west contrast; in the western area, the CO_2 fluxes were constant against latitude (west of 145°E), whereas in the eastern area, the CO_2 fluxes became more negative from south to north.

The CO_2 fluxes in 2000 showed a seasonal variation (Table 2). The variation was close to ca. 0 Gt-C yr^{-1} during the summer season and ca. $-0.4 \text{ Gt-C yr}^{-1}$ during the winter season, resulting in an annual mean value of $-0.2 \text{ Gt-C yr}^{-1}$. In the western part of the North Pacific, large negative values of $\Delta p\text{CO}_2$ and high wind speed occurred during the winter season, and the opposite conditions occurred during the summer season. These differences in conditions led to large seasonal variations in the CO_2 fluxes, ranging from 0 to $-0.4 \text{ Gt-C yr}^{-1}$ (Table 2). The peak-to-trough amplitude of CO_2 fluxes in the area could affect the seasonal variation in atmospheric CO_2 up to $\sim 0.2 \text{ ppm}$.

According to an IPCC report (2001), the oceanic CO_2 uptake over the 1990s was about 1.7 Gt-C yr^{-1} based on measurements of atmospheric O_2/N_2 . The surface area examined in this work is about 1.6% of the global ocean, but the CO_2 flux between the sea and the air corresponds to about 10% of the annual oceanic CO_2 uptake in the global ocean over the 1990s. In other words, the study area could decrease atmospheric CO_2 by $\sim 0.1 \text{ ppm}$ every year.

5. Concluding remarks

We have found that the transitional area between the subtropical and subarctic gyres in the western North Pacific ($30\text{--}40^\circ\text{N}$, $140^\circ\text{E}\text{--}180^\circ$) significantly contributes to the absorption of atmospheric CO_2 in spite of its relatively small area. This is probably because the area includes the Kuroshio Extension, which is one of the strongest sinks in the global ocean (Takahashi *et al.*, 2002). These results suggest the efficient uptake of CO_2 associated with the formation of North Pacific Subtropical Mode Water in this area. On this account, monitoring of $p\text{CO}_2^{\text{sea}}$ and related properties in this area should be intensified.

We have already confirmed that the data we obtained using the voluntary observation ship are of good quality. These data could be combined with data obtained by the RV

Table 2 Seasonal variations in air–sea fluxes of CO_2 (Gt-C yr^{-1}) in the western part of the North Pacific ($30\text{--}40^\circ\text{N}$, $140^\circ\text{E}\text{--}180^\circ$, $4.89 \times 10^6 \text{ km}^2$) in 2000

Month	$\Delta p\text{CO}_2$ (μatm)	Wind speed (m s^{-1})	CO_2 flux (Gt-C yr^{-1})*
January	−54.3	9.3	-0.32 ± 0.05
February	−50.2	11.2	-0.44 ± 0.06
March	−51.5	10.7	-0.40 ± 0.06
April	−57.8	7.9	-0.24 ± 0.05
May	−56.3	7.1	-0.20 ± 0.05
June	−44.5	6.6	-0.14 ± 0.05
July	−20.3	6.2	-0.06 ± 0.04
August	1.8	5.2	0.00 ± 0.04
September	−2.3	6.4	-0.01 ± 0.04
October	−22.5	7.0	-0.08 ± 0.05
November	−40.0	8.2	-0.19 ± 0.05
December	−50.3	9.8	-0.34 ± 0.05
Annual mean	−37.4	8.0	-0.20 ± 0.05

*The uncertainty was estimated based on the $p\text{CO}_2^{\text{sea}}$ –SST relationship and wind speed (Kalnay *et al.*, 1996).

Ryofu-maru, which provided data for secular changes in $p\text{CO}_2^{\text{sea}}$ (Inoue *et al.*, 1995). Thus, using voluntary observation ships, it may be possible to quantify temporal changes in the basin-scale oceanic uptake of CO_2 .

$p\text{CO}_2^{\text{sea}}$ was controlled primarily by the thermodynamic effects of the SST in the subtropical gyre, where nutrients were almost depleted, whereas we observed differences in $p\text{CO}_2^{\text{sea}}$ variation between the western and eastern subtropical regions. In the transitional area, the temporal and spatial variations of $p\text{CO}_2^{\text{sea}}$ were affected not only by thermodynamic effects but also by biological activity or entrainment. We interpreted these variations in terms of their relationship to variations of nutrient concentrations. Thus an elaborate system needs to be developed that can simultaneously measure both $p\text{CO}_2$ and CO_2 -related properties. More investigations using such a system are needed to elucidate the processes controlling the variations in the surface carbonate system over the North Pacific.

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篤志観測船「ありげーたりばてい」により観測された

北太平洋の大気および海水中二酸化炭素分圧

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篤志観測船「ありげーたりばてい」の北太平洋航路上（主に北緯 30～40 度）において、海水（ $p\text{CO}_2^{\text{sea}}$ ）および大気中の二酸化炭素分圧（ $p\text{CO}_2^{\text{air}}$ ）の観測を 1999 年 1 月から 2000 年 10 月までの期間に 9 回行った。 $p\text{CO}_2^{\text{sea}}$ と $p\text{CO}_2^{\text{air}}$ の観測結果から、180 度以西の海域では 8 月を除いた期間、海洋は大気から二酸化炭素を吸収しており、一方西経 160 度以東では、11 月から 5 月の期間に吸収域となっていた。西部海域においては、4～6 月に全炭酸が東部海域に比べてより大きく減少したと見積もられた。この全炭酸の減少は硝酸・亜硝酸イオンの減少とよく対応しており、両者の比率が $\text{C/N} = 9.5$ であったことから、生物活動の影響によるものと考えられた。観測された $p\text{CO}_2^{\text{sea}}$ と表面水温との関係を利用して、西部海域における 2000 年の月別二酸化炭素フラックスを評価した。当該海域は、夏には $\sim 0.4 \text{ GtC yr}^{-1}$ 、冬には $\sim 0.4 \text{ GtC yr}^{-1}$ 、年平均で 0.2 GtC yr^{-1} の二酸化炭素を大気から吸収したと見積もられた。この年間吸収量は、1990 年代に全海洋が年間吸収した二酸化炭素のおよそ 10% に相当する。

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