Western Pacific Air-Sea Interaction Study,
Eds. M. Uematsu, Y. Yokouchi, Y. W. Watanabe, S. Takeda, and Y. Yamanaka, pp. 151–161.

doi:10.5047/w-pass.a02.004

Temporal and Spatial Variations in Carbonate System and Air-Sea CO_2 Flux in the Kuroshio and Kuroshio Extension

H. Yoshikawa-Inoue[1], T. Midorikawa[2] and T. R. Takamura[3]

[1]*Faculty of Environmental Earth Science, Hokkaido University, Kita 10, Nishi 5, Kita-ku, Sapporo, Hokkaido 060-0810, Japan*
[2]*Geochemical Research Division, Meteorological Research Institute, 1-1 Nagamine, Tsukuba, Ibaraki 305-0052, Japan*
[3]*Bioscience Group, National Institute of Polar Research, 10-3, Midori-cho, Tachikawa, Tokyo 190-8518, Japan*
**E-mail: hyoshika@ees.hokudai.ac.jp*

Keywords: pCO_2; Air-sea CO_2 Flux; Kuroshio; Kuroshio Extension; pH; Carbonate System

Introduction

Because the subtropics occupies a large area of the Pacific Ocean, it is one of the important areas where the air-sea CO_2 flux, and the factors controlling this, should be clarified. In the western North Pacific subtropical gyre is the Kuroshio, known as a western boundary current. The Kuroshio carries relatively warm and salty water from the south. South of the Kuroshio extension front, subtropical mode water forms by significant deepening of the mixed layer in winter (Suga and Hanawa 1990), and the formation, and transport, of mode water play an important role in the uptake of anthropogenic CO_2 (Sabine *et al*. 2004; Rodgers *et al*. 2008). The Oyashio-Kuroshio transition region lies to the north of the Kuroshio extension front, which is influenced by both the Kuroshio and the Oyashio. In the Oyashio-Kuroshio transition region there are irregularly distributed eddies and thermohaline fronts (Kawai 1972). In the eastern North Pacific subtropical gyre, the California current, affected by cold and fresh subarctic water, flows southward. Along the shore of North America, the coastal upwelling enhances biological production due to the supply of nutrients from subsurface layers to the upper layer (Wooster and Reid 1963).

The difference in the partial pressure of CO_2 between the sea surface and the overlying air is one of the factors controlling the air-sea CO_2 flux. Compared with the partial pressure of CO_2 in the air (pCO_2^{air}), the partial pressure of CO_2 in surface seawater (pCO_2^{sea}) varies largely, both in time and space. Therefore, it is the pCO_2^{sea} that determines the direction of the CO_2 flux between the sea surface and the air. By compiling numerous pCO_2^{sea} data, Takahashi *et al*. (2009) have reported that the western North Pacific (WNP) is the area where the greatest air-sea CO_2 flux (oceanic CO_2 uptake) occurred in the Pacific Ocean, while the eastern North Pacific (ENP) is a weak sink for atmospheric CO_2. In the Kuroshio extension, Ogawa *et al*. (2006) confirmed a large air-sea CO_2 flux in 1999 and 2000 based on the voluntary observation ship pCO_2^{sea} data. In the area including the Kuroshio extension (30–40°N, 150–180°E), Takahashi *et al*. (2006) reported low decadal rates of change in

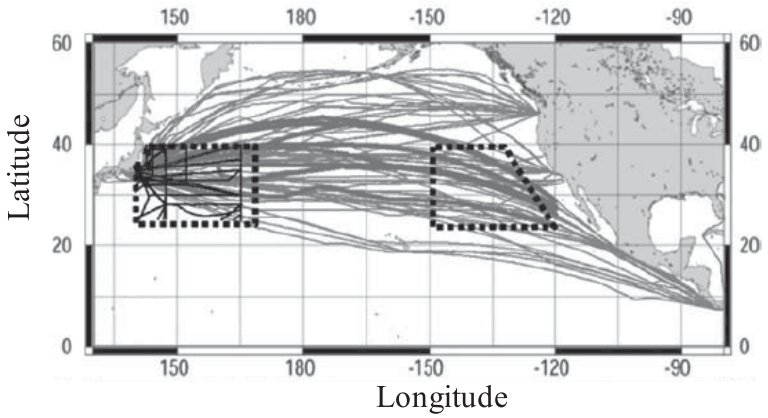

Fig. 1. Map of the study area in the North Pacific. The area surrounded by the black dotted line in each panel shows the WNP and ENP. Cruise tracks of M/S *Alligator Liberty*, M/S *Pyxis* (gray line), and R/V *Ryofu Maru* (thin black line).

pCO_2^{sea} (7–9 μatm decade^{-1}). At the same latitudes in the eastern North Pacific, they reported a wide decadal rate of change in pCO_2^{sea} (2–17 μatm decade^{-1}). Inoue *et al*. (1995), and Midorikawa *et al*. (2006), reported a growth rate of pCO_2^{sea} that is nearly equal to that of pCO_2^{air} in the western North Pacific. These two estimates will lead to a large uncertainty in the estimation of air-sea CO_2 flux in the future.

In this work, we examined seasonal/inter-annual variations in pCO_2^{sea} and air-sea CO_2 flux in the mid-latitudes of the western and eastern North Pacific based on pCO_2^{sea} and pCO_2^{air} data from 1999 to 2006 (Takamura *et al*. 2010). The pCO_2^{sea} and pCO_2^{air} were measured onboard the voluntary observation ship M/S *Alligator Liberty* (Mitsui O.S.K. Lines, Ltd.) and M/S *Pyxis* (Toyofuji Shipping Co., Ltd.). Nine crossings were operated by M/S *Alligator Liberty* between Tokyo, Japan, and Manzanilo, Republic of Panama, from January 1999 to October 2000. M/S *Pyxis* has two major sailing routes: one from Toyohashi, Japan to Portland, Oakland, and Long Beach, USA, and the other to the East Coast, USA via the Panama Canal. For our analysis, we used pCO_2^{sea} data during 62 crossings from July 2002 to April 2006. In addition to these pCO_2^{sea} and pCO_2^{air} data, we used data measured onboard the R/V *Ryofu-maru* and the R/V *Keifu-maru* belonging to the Japan Meteorological Agency (JMA). The Meteorological Research Institute, and the JMA, have been conducting observations of pCO_2^{sea} and pCO_2^{air} in the western North Pacific (along 137°E) at almost the same time of the year: from late January to early February since the early 1980s, and in June and July since 1990s.

In this work, by taking into account the frequency of the observations, and the physical/chemical properties of water, we determined the area of the WNP as 25–40°N, 140–170°E (5.0×10^6 km^2) and that of the ENP as 25–40°N, 120–150°W (4.4×10^6 km^2) (Fig. 1). The uptake of anthropogenic CO_2 leads to changes in the chemical equilibrium of the carbonate system in the surface ocean (IPCC 2007) because CO_2 acts as a weak acid in aqueous solution. The ocean acidification, due to the increase in CO_2 concentration in surface seawater, has been discussed recently, with the main focuses on the potential effects on marine ecosystems, as well as the buffer

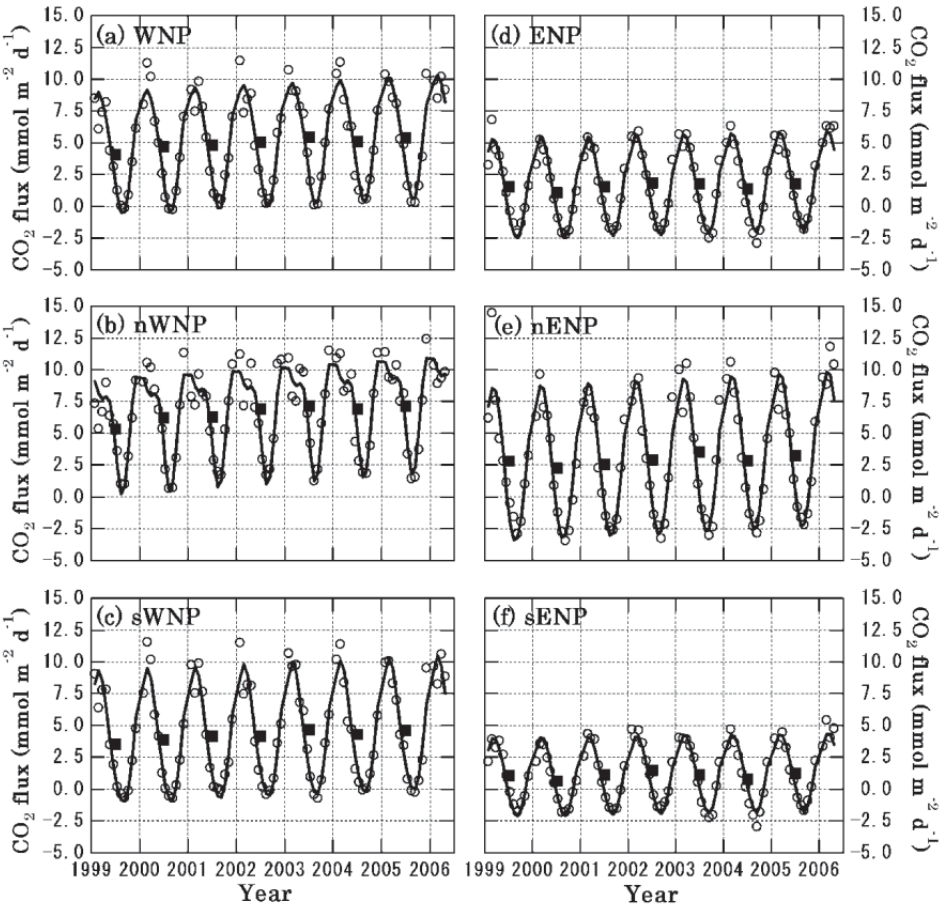

Fig. 2. Temporal variation in air-sea CO_2 flux in the (a) WNP, (b) north of 35°N in the WNP (nWNP), (c) south of 35°N in the WNP (sWNP), (d) ENP, (e) north of 35°N in the ENP (nENP), and (f) south of 35°N in the ENP (sENP) during the period from 1999 to 2006. An open circle indicates the monthly air-sea CO_2 flux, and a solid square indicates the annual mean ΔpCO_2. The black line shows the result calculated by Eq. (3) (Takamura *et al*. 2010).

capacity of the ocean. We also examined the changes of the carbonate system in the western North Pacific based on repeated measurements of the surface carbonate system. The data used in this work are available from the World Data Center for Greenhouse Gases, World Meteorological Organization, (WMO WDCGG, Tokyo, Japan, http://gaw.kishou.go.jp/wdcgg/) and the Carbon Dioxide Analysis Center (CDIAC, Oak Ridge, USA, http://cdiac.ornl.gov/oceans/).

Methods

In order to evaluate the temporal and spatial variations in pCO_2^{sea} and the air-sea CO_2 flux over the wide area of the subtropics, first we examined the interpolation/extrapolation schemes which use the commonly-available data. Historically, pCO_2^{sea} is expressed as a function of sea surface temperature (SST) based on the assumption that, either directly or indirectly, the temperature relates to the ocean

Table 1. Regression equations expressing pCO_2^{sea} as a function of SST, SSS and *t* in the WNP and ENP in 1999 and 2006. *t* is the elapsed time (month) since January 1999 (Takamura *et al.* 2010).

	Equation	*r*	rms	*n*
WNP	$pCO_2^{sea} = -4.93SST + 0.0363t + 389.8$ (<17.5 °C)	0.65	±13.8	5713
	$pCO_2^{sea} = 6.69SST + 0.0629t + 180.1$ (≥17.5°C)	0.86	±12.4	23458
	$pCO_2^{sea} = -5.62SST + 10.9SSS + 0.0071t + 26.50$ (<17.5 °C)	0.68	±13.4	5713
	$pCO_2^{sea} = 6.57SST - 8.93SSS + 0.0854t + 490.7$ (≥17.5°C)	0.86	±12.1	23458
ENP	$pCO_2^{sea} = 4.60SST - 0.0939t + 286.3$	0.50	±21.9	12776
	$pCO_2^{sea} = 9.85SST - 30.7SSS - 0.0165t + 1220$	0.89	±11.3	12776

dynamics (lateral transport, vertical mixing and upwelling), biological activities, and thermodynamics (Lee *et al.* 1998), which are the major processes controlling pCO_2^{sea}. In the WNP, a minimum pCO_2^{sea} occurred at SST of 17.5°C which was located at 32°N in winter (data not shown). The SST that occurred at the minimum pCO_2^{sea} was consistent with the winter temperature of the Kuroshio front, the boundary between the subtropical gyre and the Oyashio-Kuroshio transition region. The pCO_2^{sea} is negatively correlated with SST in the lower SST region north of the minimum pCO_2^{sea}, and positively in the higher SST region south of the minimum pCO_2^{sea}. The pCO_2^{sea} in the Oyashio region showed a large decrease from winter to spring (Midorikawa *et al.* 2003), and reached a minimum in early summer, and a secondary minimum in fall (Chierici *et al.* 2006), which is caused by the supply of CO_2-rich subsurface water via the vertical mixing/entrainment and the large biological production in spring following the SST rise. A negative pCO_2^{sea}-SST relationship north of the minimum pCO_2^{sea} is caused by the larger effect of biological activity and vertical/horizontal mixing, than the thermodynamic temperature effect on pCO_2^{sea} reported to be $4.23\%°C^{-1}$ (Takahashi *et al.* 1993), and thus north of the minimum pCO_2^{sea} is identified to be the Oyashio-Kuroshio transition region of the WNP. In the subtropics, the thermodynamic temperature effect is reportedly a major factor in pCO_2^{sea} variations (Weiss *et al.* 1982; Tans *et al.* 1990; Inoue *et al.* 1995). Therefore, south of the minimum pCO_2^{sea}, showing a positive pCO_2^{sea}-SST relationship, is identified to be the subtropical region of WNP.

The ENP is the region which has subtropical features even in the northern area, as can be expected from the low surface chlorophyll density (Polovina *et al.* 2001) and low concentration of nutrients (Ogawa *et al.* 2006). However, in the ENP, the variation of pCO_2^{sea} is not definitely expressed by the SST (Fig. 2; Stephens *et al.* 1995; Landrum *et al.* 1996). In the ENP, sea surface salinity (SSS) varied largely compared with that of the WNP. In addition to SST, SSS could assist to predict pCO_2^{sea} because salinity also relates to the ocean dynamics, the dilution/condensation of the total dissolved inorganic carbon (TCO_2) and the total alkalinity (A_T), and variations in the solubility of CO_2 and the equilibrium constants of carbonic acid.

In the ENP and WNP, we examined the relationship between pCO_2^{sea} and SST and SSS. We found that the linear function of SST, SSS, and the time (*t*) which was introduced to express the temporal variation, fitted well the observed data, better than the pCO_2^{sea}-SST relationship (Table 1):

Table 2. Growth rate of pCO_2^{sea}, ΔpCO_2, and air-sea CO_2 flux in the WNP and ENP during the period from 1999 to 2006 (Takamura *et al.* 2010).

	pCO_2^{sea} (μatm yr^{-1})	ΔpCO_2 (μatm yr^{-1})	CO_2 flux (mmol m^{-2} d^{-1} yr^{-1})
WNP	0.53 ± 0.11	1.28 ± 0.11	0.19 ± 0.05
nWNP*	0.65 ± 0.17	1.17 ± 0.17	0.26 ± 0.06
sWNP*	0.48 ± 0.13	1.34 ± 0.13	0.16 ± 0.05
ENP	1.32 ± 0.16	0.50 ± 0.16	0.09 ± 0.03
nENP*	1.13 ± 0.19	0.72 ± 0.23	0.18 ± 0.07
sENP*	1.39 ± 0.18	0.43 ± 0.18	0.05 ± 0.03

*nWNP and nENP mean the regions north of 35°N, sWNP and sENP south of 35°N.

$$pCO_2^{sea} = a_0 + a_1 SST + a_2 SSS + a_3 t, \quad (1)$$

where t denotes the elapsed time (month) since January 1999, and a_j and t are constants that are determined by the least-squares method. In the ENP, adding SSS to the equation as a variable, provides the largest improvement in the overall correlation.

The air-sea CO_2 flux (F) was calculated from the gas-transfer velocity (k_s), the solubility of CO_2 in seawater (α, Weiss 1974), and the $\Delta pCO_2 = pCO_2^{air} - pCO_2^{sea}$ (hereafter, a positive value indicates an oceanic sink for atmospheric CO_2):

$$F = k_s \alpha \Delta pCO_2. \quad (2)$$

We used a quadratic function of wind speed by Sweeney *et al.* (2007), because it has been reported to yield piston velocity values consistent with those obtained from some small-scale deliberate tracer studies, and with the total bomb-^{14}C inventory obtained for the stratosphere and troposphere. Sweeney *et al.* (2007) reported a 33% lower globally-averaged gas-transfer velocity for CO_2, as compared with that of Wanninkhof (1992) which was commonly used for the air-sea CO_2 flux estimation. By using the updated wind speed, Takahashi *et al.* (2009) have derived a gas-transfer velocity which is 4% lower than that of Sweeney *et al.* (2007). We obtained the gridded data (1° by 1°) of pCO_2^{sea} in the WNP and ENP by using SST and SSS fields. The weekly temperature and salinity data of the NCEP Pacific Ocean Analysis (http://www.cdc.noaa.gov/cdc/data.ncep.pac.ocean.html) were used to calculate the monthly mean pCO_2^{sea}. The monthly wind-speed data were taken from the reanalysis done by NCEP/NCAR (http://www.cdc.noaa.gov/cdc/data.ncep.reanalysis.derived.surface.html).

The temporal variation in the monthly mean pCO_2^{air} in the WNP and ENP was fitted to a harmonic function $f(t)$:

$$f(t) = b + \sum_{i=1}^{2} \left\{ c_i \cos\left(\frac{2\pi i}{12} t\right) + d_i \sin\left(\frac{2\pi i}{12} t\right) \right\} + et. \quad (3)$$

In Eq. (3), b, c_i, d_i and e are constants determined by the least squares method. After calculating the monthly ΔpCO_2, the ΔpCO_2 data were fitted to Eq. (3) again ($f(t) = \Delta pCO_2(t)$).

In this work, we have evaluated the pH values in the western North Pacific (along 137°E, 3–35°N) during the period from

1983 to 2008, based on measurements of pCO_2^{sea}. Over the period 1983 to 1993, pH values were calculated by the method of Dickson *et al.* (2007), by using the pCO_2^{sea}, SST, SSS data measured by MRI/JMA, and A_T was estimated to be 2295 μmol kg^{-1} at SSS = 35. The A_T value at the ambient SSS was estimated by assuming a linear proportionality to SSS. In this work, the pH values were expressed as the total hydrogen ion scale (Dickson *et al.* 2007). After 1994, when pCO_2^{sea}, SST, SSS, and TCO_2, were measured, the pH value was calculated using these four variables. As mentioned above, we used α given by Weiss (1974), and dissociation constants of carbonic acid from Lueker *et al.* (2000). Along the repeat hydrographic line at 137°E, the calculated A_T at SSS = 35 ranged from 2294 ± 4 to 2298 ± 3 μmol kg^{-1} in winter, and 2289 ± 7 to 2296 ± 8 μmol kg^{-1} in summer, for the past 14 yr, which suggests that A_T at SSS = 35 is almost constant both spatially (3–35°N) and temporally (Midorikawa *et al.* 2010). During the period from 2003 to 2008, when the pH was measured along with pCO_2^{sea}, TCO_2, SST, and SSS, the pH in surface seawater was calculated by using these variables, and was compared with the measured value. The calculated pH values agreed very well with those observed, within 0.0026 ± 0.0050 in winter, and 0.0003 ± 0.0052 in summer. The estimation of pH by this different method will allow us to evaluate the long-term change in pH in the western North Pacific.

Results and Discussion

pCO_2^{sea} in the Kuroshio and Kuroshio extension

Usually, ΔpCO_2 in the subtropical area of the WNP (south of 35°N), and the ENP, occurred as a minimum in summer (August/September), and a maximum in late-winter (March) (data not shown). In the Oyashio-Kuroshio transition area (north of 35°N), ΔpCO_2 showed two minima, in summer (August/September) and late-winter (February/March), and two maxima in late-spring (May/June) and late-fall (November/December). In the subtropics of the WNP, the pCO_2^{sea} was slightly larger than the pCO_2^{air} in summer, whilst, in the Oyashio-Kuroshio transition area of the WNP, the pCO_2^{sea} was always lower than pCO_2^{air}. In the ENP, ΔpCO_2 was less than –20 μatm, and hence, the ENP acts as a source for atmospheric CO_2 in the summer. Table 2 shows increasing rates in pCO_2^{sea} in the WNP and ENP from 1999 to 2006. In the WNP, the pCO_2^{sea} south of 35°N, assumed to be subtropical area, increased at a rate of 0.48 ± 0.13 μatm yr^{-1}, and, north of 35°N 0.65 ± 0.17 μatm yr^{-1}, the pCO_2^{sea} increased at 0.53 ± 0.11 μatm yr^{-1} for the WNP over the same period, significantly slower than those of the increase rate of pCO_2^{air} (1.81 ± 0.01 μatm yr^{-1}). Consequently, ΔpCO_2 has increased at 1.28±0.11 μatm yr^{-1} in the WNP, suggesting the possibility of an increasing CO_2 uptake. In the western North Pacific (137°E), Inoue *et al.* (1995, 1999), and Midorikawa *et al.* (2006), reported the growth rate of pCO_2^{sea} which was nearly equal to that of pCO_2^{air}. The growth rate of pCO_2^{sea} was within the range from 1.4 ± 0.2 to 1.8 ± 0.2 μatm yr^{-1} with an average of 1.6 ± 0.2 μatm yr^{-1} in winter, and from 0.8 ± 0.4 to 2.2 ± 0.4 μatm yr^{-1} with a mean value of 1.4 ± 0.3 μatm yr^{-1} in summer, over the period from 1983 to 2008 (Midorikawa *et al.* 2010). Increases in pCO_2^{sea} were mostly caused by the anthropogenic CO_2 uptake, and, to a lesser amount, by the factors controlling pCO_2^{sea} mentioned above. Along 137°E, the pCO_2^{sea} has been increasing accompanied by relatively large inter-annual variations from subtropical to equatorial regions. The inter-annual variability of pCO_2^{sea} was relatively large at latitudes south of 20°N in winter, and north of 24°N in summer. The magnitude of the inter-annual variabil-

ity in summer was larger than that of winter, especially in the region of higher SST from 25 to 31°N. Takahashi *et al*. (2006) reported relatively low growth rates of pCO_2^{sea} (7.3–8.8 μatm decade^{-1}) in the western temperate zone (30–40°N, 150–180°E), which includes the Kuroshio extension. They discussed the effects of the outflow from the Sea of Okhotsk with a negative growth rate via the Oyashio Current, and/or from the East China Sea with a higher total alkalinity. As aforementioned, A_T along 137°E remains constant over a few decades, suggesting the influence of the Sea of Okhotsk. In the ENP, the annual average of pCO_2^{sea} increased at the rate of 1.32 ± 0.16 μatm yr^{-1}, which is nearly equal to that of Takahashi *et al*. (2006) who reported 15.4–17.1 μatm decade^{-1} in the 30–40°N, 130–150°W region. In Table 1, the linear time variation term in Eq. (1) gives the increase rate of pCO_2^{sea} at given SST and SSS. However, this coefficient itself is not a robust predictor of the long-term trend of pCO_2^{sea} in the WNP and ENP because year-to-year changes in SST and SSS could affect pCO_2^{sea}. For instance, at station ALOHA (22°45′ N, 158°00′ W), a large year-to-year increase in pCO_2^{sea} occurred along with SSS, which was caused by a reduction in rainfall (Dore *et al*. 2003) and the effect of a water mass exchange accompanied by a systematic large-scale shift of the North Pacific climate system (Keeling *et al*. 2004). The increasing rate of pCO_2^{sea} estimated by the linear term in Eq. (1) (Table 1) deviates from an increasing rate at a fixed geographical position (Table 2), especially in the ENP, where the SST is a predominant factor for the inter-annual variation in pCO_2^{sea}.

Air-sea CO_2 flux

Figure 2 shows variations in the air-sea CO_2 flux in the WNP and ENP, over the period 1999 to 2006. In the WNP, air-sea CO_2 flux occurred at its minimum within the range from –0.2 to 0.6 mmol m^{-2} d^{-1} in August/September following a ΔpCO_2 minimum, and a maximum within the range from 8.2 to 11.4 mmol m^{-2} d^{-1} in January/February, which is two to three months earlier than that of ΔpCO_2. The maximum air-sea CO_2 flux varied more largely from year to year compared with the minimum flux. In winter, air-sea CO_2 flux in the Oyashio-Kuroshio transition area (north of 35°N) of WNP showed a pattern different from that of ΔpCO_2, due to a relatively high wind speed. In the ENP, the seasonal variation of air-sea CO_2 flux is at a minimum within the range from –2.9 to –1.8 mmol m^{-2} d^{-1} in August/September, and a maximum within the range from 5.2 to 6.8 mmol m^{-2} d^{-1} in January/February (Fig. 2), which is one to two months earlier than that of ΔpCO_2. The annual mean CO_2 uptake rate in the Oyashio-Kuroshio transition area (north of 35°N) is generally more than 1.5 times larger than that of the subtropical area in WNP. In the ENP, the CO_2 uptake rate north of 35°N is, on average, 2.8 times larger than that south of 35°N. During 1999 to 2006, the annual mean of the air-sea CO_2 flux increased at the rate of 0.19 ± 0.05 mmol m^{-2} d^{-1} yr^{-1} within the range from 4.1 to 5.5 mmol m^{-2} d^{-1} in the WNP, and 0.09 ± 0.03 mmol m^{-2} d^{-1} yr^{-1} within the range from 1.1 to 1.9 mmol m^{-2} d^{-1} in the ENP (Table 2). In the WNP, ΔpCO_2 in the subtropics south of 35°N increased at a rate similar to that of the Oyashio-Kuroshio transition area. The air-sea CO_2 flux in the Oyashio-Kuroshio transition area (0.26 ± 0.06 mmol m^{-2} d^{-1} yr^{-1}) increased more largely compared with that of the subtropics (0.16 ± 0.05 mmol m^{-2} d^{-1} yr^{-1}). In the ENP, the ΔpCO_2 south of 35°N increased at a rate of 0.43 ± 0.18 μatm yr^{-1} and, north of 35°N, 0.72 ± 0.23 μatm yr^{-1}. The air-sea CO_2 flux south of 35°N increased at the rate of 0.05 ± 0.03 mmol m^{-2} d^{-1} yr^{-1} and north of 35°N 0.18 ± 0.07 mmol m^{-2} d^{-1} yr^{-1}. In the north of 35°N of ENP, wind

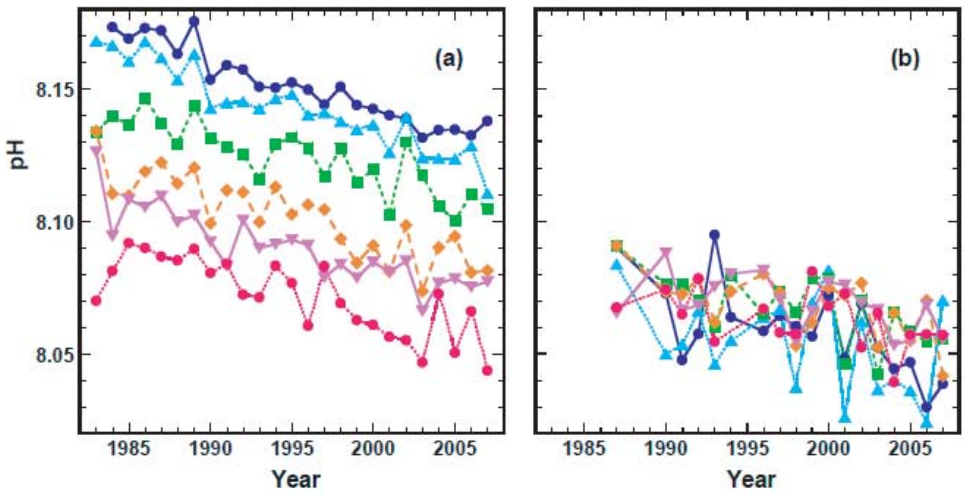

Fig. 3. Time series of pH at ambient SST at six latitudes along 137°E in (a) winter, and (b) summer. Red circles show the data at 3°N, violet triangles at 10°N, orange diamonds at 15°N, green squares at 20°N, light blue triangles at 25°N, and blue circles at 30°N (Midorikawa *et al.* 2010).

speed reveal largest increasing rate of 0.15 ± 0.08 m s^{-1} yr^{-1} in fall, that is relatively low ΔpCO_2 season in this region, than any other part and season in our studied area.

In the ENP, increases in SST over the years, and the change of wind speed, also indicate a possible linkage to the pattern of Pacific climate variability: Pacific Decadal Oscillation (PDO; Zhang *et al.* 1997; Mantua *et al.* 1997). The monthly PDO index, defined as the leading principal component of the North Pacific monthly SST variability, showed a negative phase start in July 1998, which turned to a positive phase in August 2002 (http://jisao.washington.edu/pdo/), as a result of which we could expect increases in SST and wind speed during the observation period. Larger effects of PDO on the carbonate system can be expected in the eastern North Pacific, as found in the correlation between the northeast Pacific marine ecosystem and phase changes in PDO (Mantua *et al.* 1997). A long-term monitoring of the carbonate system is needed for improving the understanding of variations in pCO_2^{sea} associated with PDO and global warming.

Long-term changes in pH at ambient SST

In winter, the estimated pH from 3 to 35°N along 137°E was relatively high at higher latitudes because SST decreased largely toward the north (Fig. 3). In contrast, pH at SST of 25°C ($pH_{T=25}$) was lower at high latitudes, and high at low latitudes, which is caused by the high concentration of TCO_2 at high latitudes (Ishii *et al.* 2001). In summer, the latitudinal distribution of pH was not clear, compared with that of winter, due to small latitudinal gradients of SST. The time series data of pH exhibit a clear decreasing trend in both winter and summer.

The inter-annual variation in pH was relatively large in summer. During the period 1983 to 2008, the linear long-term trend of pH at each latitude was estimated by a least squares method. The rate of pH decrease ranged from 0.0015 ± 0.0002 to

0.0021 ± 0.0002 yr^{-1} with a mean value of 0.0018 ± 0.0002 yr^{-1} in winter, and from 0.0008 ± 0.0004 yr^{-1} to 0.0019 ± 0.0005 yr^{-1} with a mean value of 0.0013 ± 0.0005 yr^{-1} in summer. In winter, these trends were significant at most latitudes south of 33°N ($p < 0.001$), and also in summer ($p < 0.05$ at 26 latitudes, $p < 0.1$ at 5 latitudes). These decreasing trends were comparable with those of the subtropics; 0.0019 ± 0.0002 yr^{-1} at HOT (Dore *et al*. 2009) and 0.0017 ± 0.0001 yr^{-1} at BATS (Bates 2007). The mean rate of the decreasing trend of $pH_{T=25}$ was estimated to be 0.0015 ± 0.0003 yr^{-1} in winter and 0.0014 ± 0.0004 yr^{-1} in summer, which were almost equal to those of the ambient SST. The small difference in the decreasing pH rate between the ambient SST and 25°C is caused by the long-term changes in SST: 0.02 ± 0.02°C yr^{-1} in winter, and -0.01 ± 0.02°C yr^{-1} in summer.

Conclusions

We have investigated the seasonal, and inter-annual, variations of the difference in the partial pressure of CO_2 between surface seawater (pCO_2^{sea}), the overlying air (pCO_2^{air}), and air-sea CO_2 flux in, mid-latitudes of the western North Pacific (WNP; 25–40°N, 140–170°E) and the eastern North Pacific (ENP; 25–40°N, 120–150°W), during the period 1999 to 2006. In the WNP and ENP, an area averaged ΔpCO_2 ($pCO_2^{air} - pCO_2^{sea}$) was a minimum in late summer (–4.6 to 6.7 μatm in the WNP and –32.5 to –20.5 μatm in the ENP), and a maximum in late winter (51.0 to 59.8 μatm in the WNP and 35.1 to 46.2 μatm in the ENP). The WNP acts as a significant sink for atmospheric CO_2 (4.1 to 5.5 mmol m^{-2} d^{-1}), while the ENP acts as a weak sink (1.1 to 1.9 mmol m^{-2} d^{-1}). Between 1999 to 2006, the pCO_2^{sea} in the WNP increased at a rate significantly lower (0.53 ± 0.11 μatm yr^{-1}) than that of pCO_2^{air} (1.81 ± 0.01 μatm yr^{-1}), and, in the ENP, slightly lower (1.32 ± 0.16 μatm yr^{-1}). The air-sea CO_2 flux increased at a rate of 0.19 ± 0.05 mmol m^{-2} d^{-1} yr^{-1} in the WNP and 0.09 ± 0.03 mmol m^{-2} d^{-1} yr^{-1} in the ENP, implying that the WNP will be a more significant sink for atmospheric CO_2. Increases in air-sea CO_2 flux during 1999 to 2006 might have a close linkage to the pattern of Pacific climate variability, such as the Pacific Decadal Oscillation (PDO). We evaluated the long-term trend of oceanic acidification in the surface seawater of the western North Pacific, using the pCO_2^{sea} data measured at the same time of the year from 1983 to 2010. The time series of pH data at ambient SST clearly showed the long-term decrease –0.01 to –0.02 per decade—which was close to the decreasing trend reported in the other subtropics (HOT and BATS sites).

Acknowledgements

We would like to thank the Japan Meteorological Agency, M.O. Ship Management Co., Ltd., Mitsui O.S.K. lines, and Toyofuji Shipping Co. Ltd. for the atmospheric/oceanic pCO_2 observations. We are also grateful to the Captain, officers and the ship crew onboard M/S *Alligator Liberty* and M/S *Pyxis* for their superb support. This research was supported in part by a Grant-in-Aid for Scientific Research, of the Ministry of Education, Culture, Sports, Science, and Technology of Japan (#19030001, #20310002), and by the "Global Environment Research Fund by the Ministry of the Environment Japan" D-0803.

References

Bates NR (2007) Interannual variability of the oceanic CO_2 sink in the subtropical gyre of the North Atlantic Ocean over the last two decades. J. Geophys. Res. **112**, C09013, doi:10.1029/2006JC003759.

Chierici M, Fransson A, Nojiri Y (2006) Biogeochemical processes as drivers of surface fCO_2 in contrasting provinces in the subarctic North Pacific Ocean. Global Biogeochem. Cycles **20**, GB1009, doi:10.1029/2004GB002356.

Dickson AG, Sabine CL, Christian JR (2007) *Guide to Best Practices for Ocean CO_2 Measurements*. PICES Special Publication 3, 191 pp.

Dore JE, Lukas R, Sadler DW, Karl DM (2003) Climate-driven changes to the atmospheric CO_2 sink in the subtropical North Pacific Ocean, Nature **424**, 754–757.

Dore JE, Lukas R, Sadler DW, Church MJ, Karl DM (2009) Physical and biogeochemical modulation of ocean acidification in the central North Pacific. Proc. Natl. Acad. Sci. **106**, 12,235–12,240.

Inoue HY, Matsueda H, Ishii M, Fushimi K, Hirota M, Asanuma I, Takasugi Y (1995) Long-term trend of the partial pressure of carbon dioxide (pCO_2) in surface waters of the western North Pacific, 1984–1993. Tellus **47B**, 391–413.

Inoue HY, Ishii M, Matsueda H, Saito S, Midorikawa T, Nemoto K (1999) Partial pressure of CO_2 in surface waters of the Pacific during 1968 to 1970: re-evaluation and comparison of data. Tellus **51B**, 830–848.

Intergovernmental Panel on Climate Change (2007) *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, UK and New York, NY, USA, 996 pp.

Ishii M, Inoue HY, Matsueda H, Saito S, Fushimi K, Nemoto K, Yano T, Nagai H, Midorikawa T (2001) Seasonal variation in total inorganic carbon and its controlling processes in surface waters of the western North Pacific subtropical gyre. Mar. Chem. **75**, 17–32.

Kawai H (1972) Hydrography of the Kuroshio Extension. p. 235–352. In *Kuroshio: Its Physical Aspects* (eds. Stommel H, Yoshida K), University of Tokyo Press, Tokyo,

Keeling CD, Brix H, Gruber N (2004) Seasonal and long-term dynamics of the upper ocean carbon cycle at Station ALOHA near Hawaii. Global Biogeochem. Cycles **18**, GB4006, doi:10.1029/2004GB002227.

Landrum LL, Gammon RH, Feely RA, Murphy PP, Kelly KC, Cosca CE, Weiss RF (1996) North Pacific Ocean CO_2 disequilibrium for spring through summer, 1985–1989. J. Geophys. Res. **101**(C12), 28,539–28,555.

Lee K, Wanninkhof R, Takahashi T, Doney SC, Feely RA (1998) Low interannual variability in recent oceanic uptake of atmospheric carbon dioxide. Nature **396**, 155–159.

Lueker TJ, Dickson AG, Keeling CD (2000) Ocean pCO_2 calculated from dissolved inorganic carbon, alkalinity, and equations for K_1 and K_2: validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium. Mar. Chem. **70**, 105–119.

Mantua NJ, Hare SR, Zhang Y, Wallace JM, Francis RC (1997) A Pacific interdecadal climate oscillation with impacts on salmon production. Bull. Am. Met. Soc. **78**, 1069–1079.

Midorikawa T, Ogawa K, Kamiya H, Hiraishi N, Umeda T, Wada A, Nemoto K, Ishii M (2003) Interannual variations of net community production and air-sea CO_2 flux from winter to spring in the western subarctic North Pacific. Tellus **55B**, 466–477.

Midorikawa T, Ishii M, Nemoto K, Kamiya H, Nakadate A, Masuda S, Matsueda H, Nakano T, Inoue HY (2006) Interannual variability of winter oceanic CO_2 and sea-air CO_2 flux in the western North Pacific for 2 decades. J. Geophys. Res. **111**, C07S02, doi:10.1029/2005JC003095.

Midorikawa T, Ishii M, Saito S, Sasano D, Kosugi N, Motoi T, Kamiya H, Nakadate A, Nemoto K, Inoue HY (2010) Decreasing pH trend estimated from 25-yr time series of carbonate parameters in the western North Pacific. Tellus **62B**, 649–659.

Ogawa K *et al.* (2006) Shipboard measurements of atmospheric and surface seawater pCO_2 in the North Pacific carried out from January 1999 to October 2000 on the voluntary observation ship MS *Alligator Liberty*. Pap. Met. Geophys. **57**, 37–46, doi:10.2467/mripapers.57.37.

Polovina JJ, Howell E, Kobayashi DR, Seki MP (2001) The transition zone chlorophyll front, a dynamic global feature defining migration and forage habitat for marine resources. Prog. Oceanogr. **49**, 469–483.

Rodgers KB, Sarmiento JL, Aumont O, Crevoiser C, de Boyer Montégut C, Metzl N (2008) A wintertime uptake window for anthropogenic CO_2 in the North Pacific. Global Biogeochem. Cycles **22**, GB2020, doi:10.1029/2006GB002920.

Sabine C *et al.* (2004) The oceanic sink for anthropogenic CO_2. Science **305**, 367–371.

Stephens MP, Samuels G, Olson DB, Fine RA, Takahashi T (1995) Sea-air flux of CO_2 in the North Pacific using shipboard and satellite data. J. Geophys. Res. **100**(C7), 13,571–13,583.

Suga T, Hanawa K (1990) The mixed layer climatology in the northwestern part of the North Pacific

subtropical gyre and the formation area of Subtropical Mode Water. J. Mar. Res. **48**, 543–566.
Sweeney C, Gloor EE, Jacobson AR, Key RM, McKinly G, Sarmiento JL, Wanninkhof R (2007) Constraining global air-sea gas exchange for CO_2 with recent bomb ^{14}C measurements. Global Biogeochem. Cycles **21**, doi:10.1029/2006GB002784.
Takahashi T, Olafsson J, Goddard JG, Chipman DW, Sutherland SC (1993) Seasonal variation of CO_2 and nutrients in the high-latitude surface oceans: A comparative study. Global Biogeochem. Cycles **14**, 1267–1281.
Takahashi T, Sutherland SC, Feely RA, Wanninkhof R (2006) Decadal change of the surface water pCO_2 in the North Pacific: A synthesis of 35 years of observations. J. Geophys. Res. **111**, C07S05, doi:10.1029/2005JC003074.
Takahashi T *et al*. (2009) Climatological mean and decadal change in surface ocean pCO_2, and net sea-air CO_2 flux over the global oceans. Deep-Sea Res. II **56**, 554–577.
Takamura RT, Inoue HY, Midorikawa T, Ishii M, Nojiri Y (2010) Seasonal and inter-annual variations in pCO_2^{sea} and air-sea CO_2 fluxes in mid-latitudes of the western and eastern North Pacific during 1999–2006: Recent results utilizing voluntary observation ships. J. Met. Soc. Jpn. **88**(6), 883–898.
Tans PP, Fung IY, Takahashi T (1990) Observational constraints on the global atmospheric CO_2 budget. Science **247**, 1431–1438.
Wanninkhof R (1992) Relationship between wind speed and gas exchange over the ocean. J. Geophys. Res. **97**, 7373–7382.
Weiss RF. (1974) Carbon dioxide in water and seawater: The solubility of a non-ideal gas. Mar. Chem. **2**, 203–215.
Weiss RF, Jahnke RA, Keeling CD (1982) Seasonal effects of temperature and salinity on the partial pressure of CO_2 in seawater. Nature **300**, 511–513.
Wooster WS, Reid JL Jr (1963) Eastern boundary currents. pp. 253–280. In *The Sea* (ed. Hill MN), Wiley Interscience, New York.
Zhang Y, Wallace JM, Battisti DS (1997) ENSO-like interdecadal variability: 1900–93. J. Climate **10**, 1004–1020.