

Western Pacific Air-Sea Interaction Study

year	2014
URL	http://hdl.handle.net/2261/58891

Temporal and Spatial Variations in Carbonate System and Air-Sea CO₂ Flux in the Kuroshio and Kuroshio Extension

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Keywords: pCO₂; Air-sea CO₂ 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 CO₂ 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 CO₂ (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 CO₂ between the sea surface and the overlying air is one of the factors controlling the air-sea CO₂ flux. Compared with the partial pressure of CO₂ in the air (pCO₂^{air}), the partial pressure of CO₂ in surface seawater (pCO₂^{sea}) varies largely, both in time and space. Therefore, it is the pCO₂^{sea} that determines the direction of the CO₂ flux between the sea surface and the air. By compiling numerous pCO₂^{sea} data, Takahashi *et al.* (2009) have reported that the western North Pacific (WNP) is the area where the greatest air-sea CO₂ flux (oceanic CO₂ uptake) occurred in the Pacific Ocean, while the eastern North Pacific (ENP) is a weak sink for atmospheric CO₂. In the Kuroshio extension, Ogawa *et al.* (2006) confirmed a large air-sea CO₂ flux in 1999 and 2000 based on the voluntary observation ship pCO₂^{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

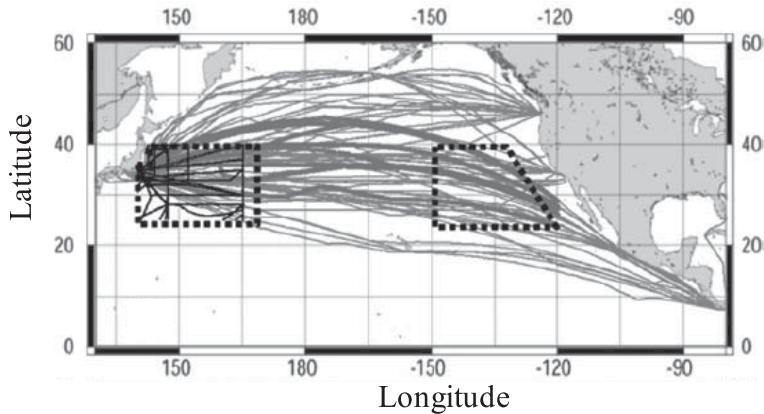


Fig. 1. Map of the study area in the North Pacific. The area surrounded by the black dotted line in each panel shows the WNP and ENP. Cruise tracks of M/S *Alligator Liberty*, M/S *Pyxis* (gray line), and R/V *Ryofu Maru* (thin black line).

$\text{pCO}_2^{\text{sea}}$ ($7\text{--}9 \mu\text{atm decade}^{-1}$). At the same latitudes in the eastern North Pacific, they reported a wide decadal rate of change in $\text{pCO}_2^{\text{sea}}$ ($2\text{--}17 \mu\text{atm decade}^{-1}$). Inoue *et al.* (1995), and Midorikawa *et al.* (2006), reported a growth rate of $\text{pCO}_2^{\text{sea}}$ that is nearly equal to that of $\text{pCO}_2^{\text{air}}$ 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 $\text{pCO}_2^{\text{sea}}$ and air-sea CO_2 flux in the mid-latitudes of the western and eastern North Pacific based on $\text{pCO}_2^{\text{sea}}$ and $\text{pCO}_2^{\text{air}}$ data from 1999 to 2006 (Takamura *et al.* 2010). The $\text{pCO}_2^{\text{sea}}$ and $\text{pCO}_2^{\text{air}}$ 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 Manzanillo, 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 $\text{pCO}_2^{\text{sea}}$ data

during 62 crossings from July 2002 to April 2006. In addition to these $\text{pCO}_2^{\text{sea}}$ and $\text{pCO}_2^{\text{air}}$ 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 $\text{pCO}_2^{\text{sea}}$ and $\text{pCO}_2^{\text{air}}$ 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 $25\text{--}40^\circ\text{N}$, $140\text{--}170^\circ\text{E}$ ($5.0 \times 10^6 \text{ km}^2$) and that of the ENP as $25\text{--}40^\circ\text{N}$, $120\text{--}150^\circ\text{W}$ ($4.4 \times 10^6 \text{ km}^2$) (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

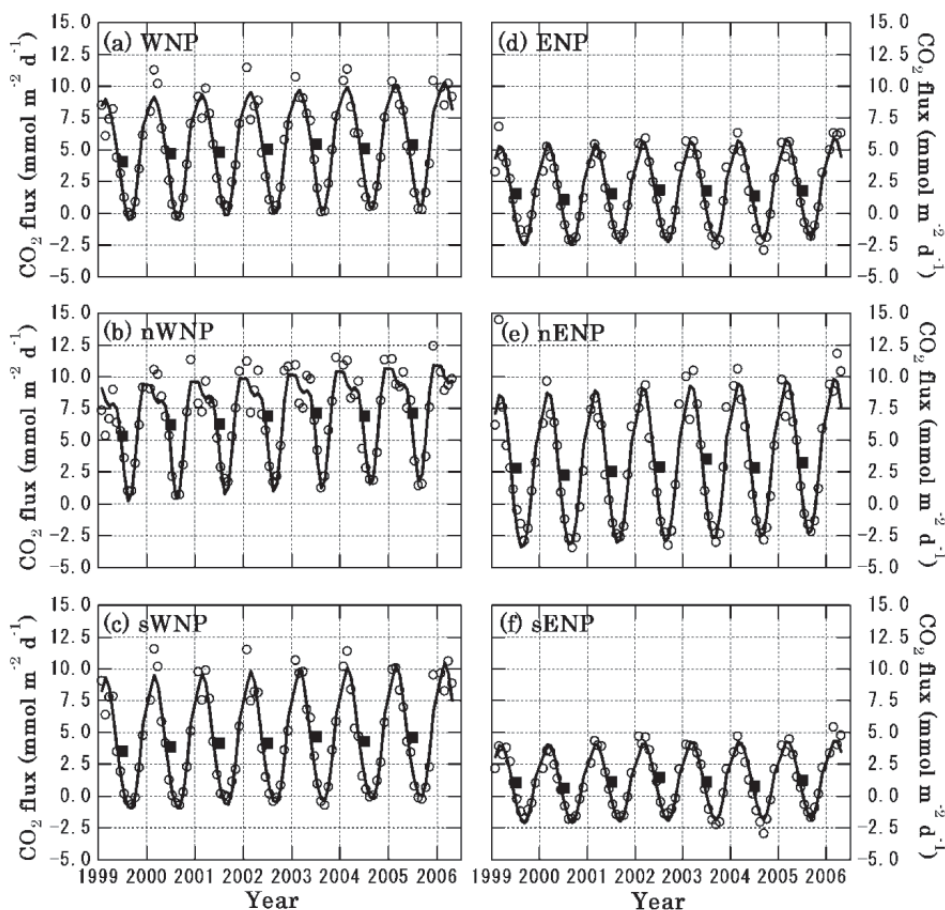


Fig. 2. Temporal variation in air-sea CO_2 flux in the (a) WNP, (b) north of 35°N in the WNP (nWNP), (c) south of 35°N in the WNP (sWNP), (d) ENP, (e) north of 35°N in the ENP (nENP), and (f) south of 35°N in the ENP (sENP) during the period from 1999 to 2006. An open circle indicates the monthly air-sea CO_2 flux, and a solid square indicates the annual mean $\Delta p\text{CO}_2$. 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 $p\text{CO}_2^{\text{sea}}$ 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, $p\text{CO}_2^{\text{sea}}$ 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 $\text{pCO}_2^{\text{sea}}$ 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	$\text{pCO}_2^{\text{sea}} = -4.93\text{SST} + 0.0363t + 389.8$ ($<17.5^\circ\text{C}$)	0.65	± 13.8	5713
	$\text{pCO}_2^{\text{sea}} = 6.69\text{SST} + 0.0629t + 180.1$ ($\geq 17.5^\circ\text{C}$)	0.86	± 12.4	23458
	$\text{pCO}_2^{\text{sea}} = -5.62\text{SST} + 10.9\text{SSS} + 0.0071t + 26.50$ ($<17.5^\circ\text{C}$)	0.68	± 13.4	5713
	$\text{pCO}_2^{\text{sea}} = 6.57\text{SST} - 8.93\text{SSS} + 0.0854t + 490.7$ ($\geq 17.5^\circ\text{C}$)	0.86	± 12.1	23458
ENP	$\text{pCO}_2^{\text{sea}} = 4.60\text{SST} - 0.0939t + 286.3$	0.50	± 21.9	12776
	$\text{pCO}_2^{\text{sea}} = 9.85\text{SST} - 30.7\text{SSS} - 0.0165t + 1220$	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 $\text{pCO}_2^{\text{sea}}$. In the WNP, a minimum $\text{pCO}_2^{\text{sea}}$ 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 $\text{pCO}_2^{\text{sea}}$ was consistent with the winter temperature of the Kuroshio front, the boundary between the subtropical gyre and the Oyashio-Kuroshio transition region. The $\text{pCO}_2^{\text{sea}}$ is negatively correlated with SST in the lower SST region north of the minimum $\text{pCO}_2^{\text{sea}}$, and positively in the higher SST region south of the minimum $\text{pCO}_2^{\text{sea}}$. The $\text{pCO}_2^{\text{sea}}$ 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 $\text{pCO}_2^{\text{sea}}$ -SST relationship north of the minimum $\text{pCO}_2^{\text{sea}}$ is caused by the larger effect of biological activity and vertical/horizontal mixing, than the thermodynamic temperature effect on $\text{pCO}_2^{\text{sea}}$ reported to be $4.23\%^\circ\text{C}^{-1}$ (Takahashi *et al.* 1993), and thus north of the minimum $\text{pCO}_2^{\text{sea}}$ 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 $\text{pCO}_2^{\text{sea}}$ variations (Weiss *et al.* 1982; Tans *et al.* 1990; Inoue *et al.* 1995). Therefore, south of the minimum $\text{pCO}_2^{\text{sea}}$, showing a positive $\text{pCO}_2^{\text{sea}}$ -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 $\text{pCO}_2^{\text{sea}}$ 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 $\text{pCO}_2^{\text{sea}}$ 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 $\text{pCO}_2^{\text{sea}}$ 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 $\text{pCO}_2^{\text{sea}}$ -SST relationship (Table 1):

Table 2. Growth rate of $p\text{CO}_2^{\text{sea}}$, $\Delta p\text{CO}_2$, and air-sea CO_2 flux in the WNP and ENP during the period from 1999 to 2006 (Takamura *et al.* 2010).

	$p\text{CO}_2^{\text{sea}}$ ($\mu\text{atm yr}^{-1}$)	$\Delta p\text{CO}_2$ ($\mu\text{atm yr}^{-1}$)	CO_2 flux ($\text{mmol m}^{-2} \text{d}^{-1} \text{yr}^{-1}$)
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 .

$$p\text{CO}_2^{\text{sea}} = a_0 + a_1\text{SST} + a_2\text{SSS} + a_3t, \quad (1)$$

where t denotes the elapsed time (month) since January 1999, and a_i 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 $\Delta p\text{CO}_2 = p\text{CO}_2^{\text{air}} - p\text{CO}_2^{\text{sea}}$ (hereafter, a positive value indicates an oceanic sink for atmospheric CO_2):

$$F = k_s \alpha \Delta p\text{CO}_2. \quad (2)$$

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 $p\text{CO}_2^{\text{sea}}$ 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 $p\text{CO}_2^{\text{sea}}$. 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 $p\text{CO}_2^{\text{air}}$ 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 $\Delta p\text{CO}_2$, the $\Delta p\text{CO}_2$ data were fitted to Eq. (3) again ($f(t) = \Delta p\text{CO}_2(t)$).

In this work, we have evaluated the pH values in the western North Pacific (along 137°E , $3\text{--}35^\circ\text{N}$) during the period from

1983 to 2008, based on measurements of $p\text{CO}_2^{\text{sea}}$. Over the period 1983 to 1993, pH values were calculated by the method of Dickson *et al.* (2007), by using the $p\text{CO}_2^{\text{sea}}$, SST, SSS data measured by MRI/JMA, and A_T was estimated to be $2295 \mu\text{mol kg}^{-1}$ at $\text{SSS} = 35$. 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 $p\text{CO}_2^{\text{sea}}$, 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 $\text{SSS} = 35$ ranged from 2294 ± 4 to $2298 \pm 3 \mu\text{mol kg}^{-1}$ in winter, and 2289 ± 7 to $2296 \pm 8 \mu\text{mol kg}^{-1}$ in summer, for the past 14 yr, which suggests that A_T at $\text{SSS} = 35$ is almost constant both spatially ($3\text{--}35^\circ\text{N}$) and temporally (Midorikawa *et al.* 2010). During the period from 2003 to 2008, when the pH was measured along with $p\text{CO}_2^{\text{sea}}$, 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

pCO₂^{sea} in the Kuroshio and Kuroshio extension

Usually, $\Delta p\text{CO}_2$ 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), $\Delta p\text{CO}_2$ 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 $p\text{CO}_2^{\text{sea}}$ was slightly larger than the $p\text{CO}_2^{\text{air}}$ in summer, whilst, in the Oyashio-Kuroshio transition area of the WNP, the $p\text{CO}_2^{\text{sea}}$ was always lower than $p\text{CO}_2^{\text{air}}$. In the ENP, $\Delta p\text{CO}_2$ was less than $-20 \mu\text{atm}$, and hence, the ENP acts as a source for atmospheric CO_2 in the summer. Table 2 shows increasing rates in $p\text{CO}_2^{\text{sea}}$ in the WNP and ENP from 1999 to 2006. In the WNP, the $p\text{CO}_2^{\text{sea}}$ south of 35°N , assumed to be subtropical area, increased at a rate of $0.48 \pm 0.13 \mu\text{atm yr}^{-1}$, and, north of 35°N $0.65 \pm 0.17 \mu\text{atm yr}^{-1}$, the $p\text{CO}_2^{\text{sea}}$ increased at $0.53 \pm 0.11 \mu\text{atm yr}^{-1}$ for the WNP over the same period, significantly slower than those of the increase rate of $p\text{CO}_2^{\text{air}}$ ($1.81 \pm 0.01 \mu\text{atm yr}^{-1}$). Consequently, $\Delta p\text{CO}_2$ has increased at $1.28 \pm 0.11 \mu\text{atm yr}^{-1}$ 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 $p\text{CO}_2^{\text{sea}}$ which was nearly equal to that of $p\text{CO}_2^{\text{air}}$. The growth rate of $p\text{CO}_2^{\text{sea}}$ was within the range from 1.4 ± 0.2 to $1.8 \pm 0.2 \mu\text{atm yr}^{-1}$ with an average of $1.6 \pm 0.2 \mu\text{atm yr}^{-1}$ in winter, and from 0.8 ± 0.4 to $2.2 \pm 0.4 \mu\text{atm yr}^{-1}$ with a mean value of $1.4 \pm 0.3 \mu\text{atm yr}^{-1}$ in summer, over the period from 1983 to 2008 (Midorikawa *et al.* 2010). Increases in $p\text{CO}_2^{\text{sea}}$ were mostly caused by the anthropogenic CO_2 uptake, and, to a lesser amount, by the factors controlling $p\text{CO}_2^{\text{sea}}$ mentioned above. Along 137°E , the $p\text{CO}_2^{\text{sea}}$ has been increasing accompanied by relatively large inter-annual variations from subtropical to equatorial regions. The inter-annual variability of $p\text{CO}_2^{\text{sea}}$ 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 $p\text{CO}_2^{\text{sea}}$ (7.3–8.8 $\mu\text{atm decade}^{-1}$) 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 $p\text{CO}_2^{\text{sea}}$ increased at the rate of $1.32 \pm 0.16 \mu\text{atm yr}^{-1}$, which is nearly equal to that of Takahashi *et al.* (2006) who reported 15.4–17.1 $\mu\text{atm decade}^{-1}$ 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 $p\text{CO}_2^{\text{sea}}$ at given SST and SSS. However, this coefficient itself is not a robust predictor of the long-term trend of $p\text{CO}_2^{\text{sea}}$ in the WNP and ENP because year-to-year changes in SST and SSS could affect $p\text{CO}_2^{\text{sea}}$. For instance, at station ALOHA (22°45' N, 158°00' W), a large year-to-year increase in $p\text{CO}_2^{\text{sea}}$ 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 $p\text{CO}_2^{\text{sea}}$ 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 $p\text{CO}_2^{\text{sea}}$.

Air-sea CO₂ flux

Figure 2 shows variations in the air-sea CO₂ flux in the WNP and ENP, over the period 1999 to 2006. In the WNP, air-sea CO₂ flux occurred at its minimum within

the range from -0.2 to $0.6 \text{ mmol m}^{-2} \text{ d}^{-1}$ in August/September following a $\Delta p\text{CO}_2$ minimum, and a maximum within the range from 8.2 to $11.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ in January/February, which is two to three months earlier than that of $\Delta p\text{CO}_2$. The maximum air-sea CO₂ flux varied more largely from year to year compared with the minimum flux. In winter, air-sea CO₂ flux in the Oyashio-Kuroshio transition area (north of 35°N) of WNP showed a pattern different from that of $\Delta p\text{CO}_2$, due to a relatively high wind speed. In the ENP, the seasonal variation of air-sea CO₂ flux is at a minimum within the range from -2.9 to $-1.8 \text{ mmol m}^{-2} \text{ d}^{-1}$ in August/September, and a maximum within the range from 5.2 to $6.8 \text{ mmol m}^{-2} \text{ d}^{-1}$ in January/February (Fig. 2), which is one to two months earlier than that of $\Delta p\text{CO}_2$. The annual mean CO₂ 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 CO₂ 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 CO₂ flux increased at the rate of $0.19 \pm 0.05 \text{ mmol m}^{-2} \text{ d}^{-1} \text{ yr}^{-1}$ within the range from 4.1 to $5.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ in the WNP, and $0.09 \pm 0.03 \text{ mmol m}^{-2} \text{ d}^{-1} \text{ yr}^{-1}$ within the range from 1.1 to $1.9 \text{ mmol m}^{-2} \text{ d}^{-1}$ in the ENP (Table 2). In the WNP, $\Delta p\text{CO}_2$ in the subtropics south of 35°N increased at a rate similar to that of the Oyashio-Kuroshio transition area. The air-sea CO₂ flux in the Oyashio-Kuroshio transition area ($0.26 \pm 0.06 \text{ mmol m}^{-2} \text{ d}^{-1} \text{ yr}^{-1}$) increased more largely compared with that of the subtropics ($0.16 \pm 0.05 \text{ mmol m}^{-2} \text{ d}^{-1} \text{ yr}^{-1}$). In the ENP, the $\Delta p\text{CO}_2$ south of 35°N increased at a rate of $0.43 \pm 0.18 \mu\text{atm yr}^{-1}$ and, north of 35°N, $0.72 \pm 0.23 \mu\text{atm yr}^{-1}$. The air-sea CO₂ flux south of 35°N increased at the rate of $0.05 \pm 0.03 \text{ mmol m}^{-2} \text{ d}^{-1} \text{ yr}^{-1}$ and north of 35°N $0.18 \pm 0.07 \text{ mmol m}^{-2} \text{ d}^{-1} \text{ yr}^{-1}$. In the north of 35°N of ENP, wind

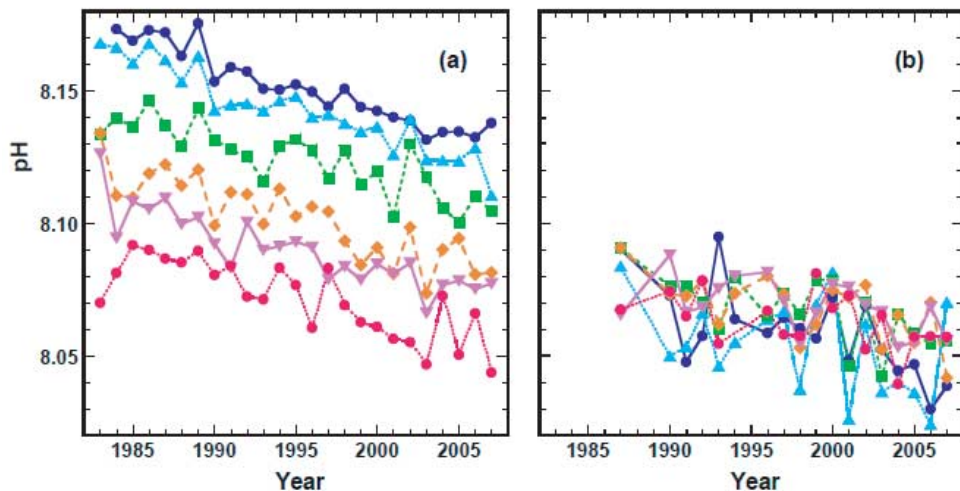


Fig. 3. Time series of pH at ambient SST at six latitudes along 137°E in (a) winter, and (b) summer. Red circles show the data at 3°N, violet triangles at 10°N, orange diamonds at 15°N, green squares at 20°N, light blue triangles at 25°N, and blue circles at 30°N (Midorikawa *et al.* 2010).

speed reveal largest increasing rate of $0.15 \pm 0.08 \text{ m s}^{-1} \text{ yr}^{-1}$ in fall, that is relatively low $\Delta p\text{CO}_2$ 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 $p\text{CO}_2^{\text{sea}}$ 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 ($\text{pH}_{T=25}$) 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

$0.0021 \pm 0.0002 \text{ yr}^{-1}$ with a mean value of $0.0018 \pm 0.0002 \text{ yr}^{-1}$ in winter, and from $0.0008 \pm 0.0004 \text{ yr}^{-1}$ to $0.0019 \pm 0.0005 \text{ yr}^{-1}$ with a mean value of $0.0013 \pm 0.0005 \text{ yr}^{-1}$ 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; $0.0019 \pm 0.0002 \text{ yr}^{-1}$ at HOT (Dore *et al.* 2009) and $0.0017 \pm 0.0001 \text{ yr}^{-1}$ at BATS (Bates 2007). The mean rate of the decreasing trend of $\text{pH}_{T=25}$ was estimated to be $0.0015 \pm 0.0003 \text{ yr}^{-1}$ in winter and $0.0014 \pm 0.0004 \text{ yr}^{-1}$ 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: $0.02 \pm 0.02^\circ\text{C yr}^{-1}$ in winter, and $-0.01 \pm 0.02^\circ\text{C yr}^{-1}$ 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 ($\text{pCO}_2^{\text{sea}}$), the overlying air ($\text{pCO}_2^{\text{air}}$), and air-sea CO_2 flux in, mid-latitudes of the western North Pacific (WNP; $25\text{--}40^\circ\text{N}$, $140\text{--}170^\circ\text{E}$) and the eastern North Pacific (ENP; $25\text{--}40^\circ\text{N}$, $120\text{--}150^\circ\text{W}$), during the period 1999 to 2006. In the WNP and ENP, an area averaged ΔpCO_2 ($\text{pCO}_2^{\text{air}} - \text{pCO}_2^{\text{sea}}$) was a minimum in late summer (-4.6 to $6.7 \mu\text{atm}$ in the WNP and -32.5 to $-20.5 \mu\text{atm}$ in the ENP), and a maximum in late winter (51.0 to $59.8 \mu\text{atm}$ in the WNP and 35.1 to $46.2 \mu\text{atm}$ in the ENP). The WNP acts as a significant

sink for atmospheric CO_2 (4.1 to $5.5 \text{ mmol m}^{-2} \text{ d}^{-1}$), while the ENP acts as a weak sink (1.1 to $1.9 \text{ mmol m}^{-2} \text{ d}^{-1}$). Between 1999 to 2006, the $\text{pCO}_2^{\text{sea}}$ in the WNP increased at a rate significantly lower ($0.53 \pm 0.11 \mu\text{atm yr}^{-1}$) than that of $\text{pCO}_2^{\text{air}}$ ($1.81 \pm 0.01 \mu\text{atm yr}^{-1}$), and, in the ENP, slightly lower ($1.32 \pm 0.16 \mu\text{atm yr}^{-1}$). The air-sea CO_2 flux increased at a rate of $0.19 \pm 0.05 \text{ mmol m}^{-2} \text{ d}^{-1} \text{ yr}^{-1}$ in the WNP and $0.09 \pm 0.03 \text{ mmol m}^{-2} \text{ d}^{-1} \text{ yr}^{-1}$ 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 $\text{pCO}_2^{\text{sea}}$ 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.

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