Long-term trend of CO$_2$ and ocean acidification in the surface water of the Ulleung Basin, the East/Japan Sea inferred from the underway observational data

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Abstract
Anthropogenic carbon is responsible for both global warming and ocean acidification. Efforts are underway to understand the role of ocean in a high CO$_2$ world on a global context. However, marginal seas received little attention despite their significant contribution to biogeochemical cycles. Here we report that the CO$_2$ increase and ocean acidification in the surface waters of the Ulleung Basin (UB) of the East/Japan Sea are much faster than the global mean, and possible causes are discussed. Fourteen observations of surface f/CO$_2$ were made in the period from 1995 to 2009. The decadal trend of f/CO$_2$ increment was estimated by harmonic analysis. The estimated rates of increase of f/CO$_2$ were 1.8 μatm yr$^{-1}$ for the atmosphere and 2.7 μatm yr$^{-1}$ for the surface ocean. The rates exceed the global mean of 1.5 μatm yr$^{-1}$. The ocean acidification trend, calculated from total alkalinity and f/CO$_2$, was estimated to be 0.03 pH units decade$^{-1}$. Surface seawater of the UB has been acidified more rapidly compared to the global mean (0.02 pH units decade$^{-1}$). Results show that, if warming strengthens the currents or advection in the marginal seas, biological pump will be enhanced. This would lead to compensation for the presumed reduction in oceanic uptake of atmospheric CO$_2$ in the warmer world, which warrants quantification worldwide.
1 Introduction

The IPCC (2007) announced that the anthropogenic CO$_2$ that has accumulated in the atmosphere since the Industrial Revolution is responsible for the enhanced greenhouse effect. The ocean is the ultimate mobile carbon storage reservoir in the Earth system. The surface ocean absorbs atmospheric CO$_2$ by means of both physical and biogeochemical processes. In the oceanic carbonate system, the dissolved carbon is transported to the deep ocean by the oceanic carbon pumps and eventually sequestrated in deep-sea sediments. Sabine et al. (2004) reported that about one-third of the CO$_2$ from the total anthropogenic CO$_2$ emissions is stored in the ocean. Currently, results from established oceanic time-series stations show that the trend of increasing CO$_2$ in surface seawater exceeds that of the atmosphere (Bates, 2001; Keeling et al., 2004) and is accelerating ocean acidification (Caldeira and Wickett, 2003; Key et al., 2004; Orr et al., 2005).

Ocean carbon uptake is commonly described as a variety of carbon pumps, which operate by thermodynamics (e.g., temperature effects on the solubility of CO$_2$), physical transport (e.g., mixing and advection of water masses carrying various forms of carbon), sinking of soft-tissue (e.g., carbon uptake/release and export by phytoplankton during photosynthesis/respiration), and sinking of carbonate shells (e.g., formation and dissolution of CaCO$_3$) (Volk and Hoffert, 1985). These processes are easily affected, directly or indirectly, by temperature. The world ocean’s temperature from the surface to 3000 m increased by 0.06 °C between the mid 1950s and mid 1990s because of an enhanced greenhouse effect (Levitus et al., 2005), and previous works have shown that the trend of increasing global sea surface temperature (SST) is about 0.08 – 0.14 °C decade$^{-1}$ (Nicholls et al., 1996; Molinari et al., 1997; Casey and Cornillon, 2001). Soaring SST creates stronger stratification between the surface sea (upper mixed layer) and the deep ocean. It might affect the great ocean conveyor system by weakening deep water formation. The warming will also weaken the solubility pump and the biological carbon pump through fortified stratification. Overall, a positive feedback exists between global warming and ocean carbon uptake, thus making the situation worse.

Nearly all the ocean’s dynamics can be observed and studied in the East/Japan Sea (EJS) despite its relatively small dimensions (Kim and Kim, 1996; Kim et al., 2001; Kang et al., 2003). The Ulleung Basin (UB), located on the western side of the southern EJS, has complex hydrography. The bifurcation of warm current entering through the Korea Strait leaves
numerous spin-off mesoscale eddies at the surface, and beneath the surface, a number of cold currents originate from the winter overturning along the Siberian coast of the EJS. Winter mode water formation is occasionally observed (Kim et al., 1991; Seung and Kim, 1993; Talley et al., 2003). The UB supports a high productivity (>220 gC m\textsuperscript{−2} yr\textsuperscript{−1}) owing to its surface dynamics and coastal upwelling (Yamada et al., 2004; Yoo and Park, 2009). Because the UB has strong solubility pumps and biological pumps, it is an ideal laboratory for ocean carbon uptake studies. For this reason some studies were carried out in the UB (Oh et al., 1999; Choi et al., 2011, 2012). In particular, it has been noted that the role of the coastal ocean in the global carbon budget has been underestimated (Wollast, 1998; Borges et al., 2005) and under debate (Cai and Dai, 2004; Thomas et al., 2004). Therefore, the role of the carbon pump in marginal seas should be reconsidered.

To reduce the scientific uncertainty in the prediction of future climate, a better understanding of the carbon flux among various reservoirs, especially the fluxes across the air-sea interface, is required. The Takahashi climatology (Takahashi et al., 2002) utilized all of the available data for modeling but still neglected marginal seas. Here, we like to emphasize the role of the marginal sea, as exemplified by the UB, and compare it to that for the entire ocean. There is no time-series station comparable to BATS or HOT in the EJS. However, we attempted to fill the gap of oceanic CO\textsubscript{2} time series in the UB by interpolation using harmonic function analysis of the data from repeated measurements. Although simplified and crude, an attempt to discern the long-term trend of CO\textsubscript{2} uptake and acidification in a marginal sea that operates its own conveyor belt at a much faster time scale than the global ocean is here made for the first time.

2 Experimental Methods and Data Analysis

2.1 Experimental methods

Measurements of the partial pressure of CO\textsubscript{2} (pCO\textsubscript{2}) in the surface water and overlying atmosphere, sea surface temperature (SST), and sea surface salinity (SSS) were carried out fourteen times in the EJS from 1995 to 2009 (Table 1). The data that were collected in the UB, the southwestern part of the EJS, were used in this study. The study area was defined as the region from 36–38 °N latitude and 130–133 °E longitude (Fig. 1).
The $pCO_2$ of surface seawater and the overlying atmosphere was measured by LiCor model 6252 non-dispersive infrared (NDIR) gas analyzer with a two-stage Weiss-type equilibrator. The $CO_2$ concentration from the NDIR was acquired every 2 seconds and, after statistical treatment for 1 minute or 2 minute, averaged data were obtained and used as the final data. Three different standard gases were used to calibrate the NDIR. Every 12 hours, a series of standard gases was analyzed for calibration; one of the standard gases was analyzed every 6 hours to check for drift of the machine. Atmospheric and surface seawater $pCO_2$ were analyzed every 15 minutes and 45 minutes on the hour, respectively. Surface seawater $pCO_2$ was analyzed by equilibrating air with surface seawater fed to the equilibrator. In-situ SST and SSS were measured using thermostalinograph (SeaBird Electronics, Model SBE-21 or SBE-45).

$\Delta fCO_2$ is defined as the difference between $fCO_2$ in the surface water ($fCO_2^{sea}$) and overlying atmosphere ($fCO_2^{atm}$) ($\Delta fCO_2 = fCO_2^{sea} - fCO_2^{atm}$). When we calculated $\Delta fCO_2$, we applied average value of prior and posterior $fCO_2^{atm}$ data to $fCO_2^{sea}$ data, since we don’t have both data at the same time and the $CO_2$ variation in the atmosphere is much smaller than in the seawater.

Total alkalinity (TA) was determined onboard by a potentiometric titration method using a closed cell (Millero et al., 1993). Total alkalinity was calibrated by Dickson’s CRMs which are measured at every cruise. The TA data were obtained during cruises 9906, 0306, 0405, and 0410 (Table 1). Surface seawater pH values were obtained immediately after sampling by a spectrophotometric method using the indicator dye $m$-cresol purple (Clayton and Byrne, 1993). The extinction coefficients for $m$-cresol purple from Clayton and Byrne (1993) were used. Determination of surface seawater pH values was carried out during cruises 9906, 0306, 0406, and 0410 (Table 1).

### 2.2 Air-sea flux estimation

The $CO_2$ flux (mmol C m$^{-2}$ d$^{-1}$) was estimated from following equation:

$$\text{Flux} = k \times s \times \Delta fCO_2$$

where $k$ is the gas transfer velocity (cm h$^{-1}$), $s$ is the solubility of $CO_2$ gas in seawater (mol kg$^{-1}$ atm$^{-1}$; Weiss, 1974). We choose the formulas for $k$ and the wind speed relationships used by Wanninkhof (1992). The NCEP wind speed data (http://www.cdc.noaa.gov/cdc/reanalysis)
averaged on monthly scale in 36 – 38 °N latitude and 130 – 133 °E longitude was used to estimate for flux.

3 Results and Discussion

3.1 General characteristics of $f_{\text{CO}_2}$ and $\text{CO}_2$ flux in the UB

The secular variation of mean $f_{\text{CO}_2}^{\text{sea}}$ and $f_{\text{CO}_2}^{\text{atm}}$ of the UB from 1995 to 2009 is shown in Fig. 2. The $f_{\text{CO}_2}^{\text{sea}}$ ranged from 125 to 499 µatm with a mean value of 350.9 µatm (sd = 41.8), and the $f_{\text{CO}_2}^{\text{atm}}$ varied from 344 to 397 µatm with a mean value of 370.5 µatm (sd = 8.7). The $f_{\text{CO}_2}^{\text{sea}}$ was generally lower than the $f_{\text{CO}_2}^{\text{atm}}$ indicating that the surface seawater was undersaturated to atmospheric $\text{CO}_2$ in this area.

The secular trend of $f_{\text{CO}_2}$ includes the long-term linear trend as well as the cyclic seasonal variation (Keeling et al., 2004). The harmonic function, which is the sum of two components defined as the one-year and half-year component, has been used primarily to reconstruct time series data. Since this analysis method was first introduced by Nojiri et al. (1999), harmonic functions have been used extensively for $f_{\text{CO}_2}$ variability studies (Zeng et al., 2002; Lüger et al., 2004; Chierici et al., 2006). We applied the harmonic function analysis to $f_{\text{CO}_2}$ data from the UB to estimate the decadal trend of $\text{CO}_2$ and to separate thermal and non-thermal effects on the $f_{\text{CO}_2}$. Because harmonic function analysis is a technique for annual data, we added the long-term linear trend to the harmonic function as follows:

$$f_{\text{CO}_2}(t) = c_0 + c_1 \times \sin(2\pi t) + c_2 \times \cos(2\pi t) + c_3 \times \sin(4\pi t) + c_4 \times \cos(4\pi t) + c_5 \times t$$

(1)

where $t$ is year.

The set of six constant coefficients, $c_0$, $c_1$, $c_2$, $c_3$, $c_4$, and $c_5$, ensured a satisfactory fit of the harmonic function of Eq. (1) to the observed data ($R^2 = 0.78$ for seawater, $R^2 = 0.96$ for air), when the constant coefficients were equal to these values (Fig. 3):

- $c_0 = -4977.46$, $c_1 = -29.97$, $c_2 = 0.88$, $c_3 = -1.45$, $c_4 = 23.41$, $c_5 = 2.66$ (for seawater),
- $c_0 = -3308.75$, $c_1 = 2.51$, $c_2 = 7.22$, $c_3 = -2.45$, $c_4 = -1.46$, $c_5 = 1.84$ (for air).

Among the results, the $c_5$ value which means annual trend for $f_{\text{CO}_2}^{\text{sea}}$ was estimated to be 2.7 µatm yr$^{-1}$ and that for $f_{\text{CO}_2}^{\text{atm}}$ was 1.8 µatm yr$^{-1}$.
The secular variation of $\Delta f/CO_2$ is shown in Fig. 4a. Although the $f_{CO_2}^{sea}$ and $f_{CO_2}^{atm}$ varies with time, the secular variation of $f/CO_2$ can be insignificant on the variation of $\Delta f/CO_2$, since $\Delta f/CO_2$ was calculated with $f/CO_2$ values in the seawater and in the atmosphere at the same time. We can hardly find the long-term trend of $\Delta f/CO_2$. However, the seasonal variation of $\Delta f/CO_2$ shows that seawater is generally undersaturated with respect to the atmosphere with exception in summer (Fig. 4b) as other studies reported (Oh et al., 1999; Choi et al., 2012). Therefore, the UB serves as a sink of atmospheric CO$_2$, in general.

The sea-air CO$_2$ fluxes in 1995 and 2004 were estimated in order to evaluate the effect of the last decadal increasing trend in $f/CO_2$. The $\Delta f/CO_2$, which estimated by The sea-air CO$_2$ fluxes were evaluated to be -0.95 ± 0.53 mol m$^{-2}$ yr$^{-1}$ for 1995 and -0.81 ± 0.49 mol m$^{-2}$ yr$^{-1}$ for 2004. This result shows that the UB acts as a carbon sink and its carbon sink efficiency in unit area is almost 1.7(±0.3)- fold higher than global ocean (-0.51 mol m$^{-2}$ yr$^{-1}$, Takahashi et al., 2002). However the flux had been decreased about 15 % during the last decade. Choi et al. (2012) and Oh et al. (1999) reported that the annual integrated CO$_2$ flux in this area was -2.47±1.26 mol m$^{-2}$ yr$^{-1}$ and -2.2 mol m$^{-2}$ yr$^{-1}$, which were larger than our results. The transiency of their observations could lead overestimation in CO$_2$ flux because of fewer observations (less than four times) despite of the complexity of the monthly variability and significant seasonal amplitude in $f/CO_2^{sea}$ in the UB.

3.2 Seasonal variability and controlling factors of $f/CO_2$ in the UB

The parameters which can control the $f/CO_2^{sea}$ such as sea surface temperature (SST), mixed layer depth (MLD) based on the climatology data (de Boyer- Montégut et al., 2004), and chlorophyll-$a$ concentration inferred from the SeaWiFS data between 1998 and 2007 are represented in Fig. 5. The SST reached a minimum in winter (February) and a maximum in summer (August and September) and had a mean value of 18.5 °C. The monthly variation in $f/CO_2^{atm}$ shows opposite in phase to that of SST. The monthly variation pattern of $f/CO_2^{atm}$ followed the general seasonal cycle of $f/CO_2$ (or $p_{CO_2}$) monitored in the North Hemisphere; i.e., the $f/CO_2^{atm}$ reached its maximum value in spring and minimum value in summer. The $f/CO_2^{sea}$, meanwhile, showed more complex variation than did the $f/CO_2^{atm}$. The monthly mean of the $f/CO_2^{sea}$ in February, March, and April was lower than the average value (350.9 µatm) but that in August and December was above the average. The May–September data were
close to the average. During the warm season (June to August), relatively high \( f\text{CO}_2^{\text{sea}} \) was associated with elevated SST. During the fall and winter (October to February), monthly \( f\text{CO}_2^{\text{sea}} \) values were higher than those in spring (April and May). This difference was a result of vertical entrainment of \( \text{CO}_2 \)-rich subsurface water despite the decreasing SST. Deepening of MLD (>50 m) supported high \( f\text{CO}_2^{\text{sea}} \) phenomenon in winter (Fig. 5b). Comparison of the normalized total \( \text{CO}_2 \) (NT\( \text{CO}_2 \)) in the EJS showed the difference of ~ 100 \( \mu \text{mol kg}^{-1} \) in surface layer between summer and winter (Park, 1997). It also could be a result of the biological drawdown of \( \text{CO}_2 \) in March and April, when the \( f\text{CO}_2^{\text{sea}} \) attained its lowest value. During March and April, satellite-based chlorophyll-\( \alpha \) concentration reached a peak value (> 1 mg m\(^{-3} \)) suggesting a possibility of biological \( \text{CO}_2 \) drawdown (Fig. 5c).

Takahashi et al. (2002) proposed a method for estimating the relative importance of the effects of biological activity and seasonal temperature change on the \( p\text{CO}_2 \) of surface seawater. In order to estimate the relative magnitude of these effects, the ratio of the thermal effect (effect of temperature change) to the non-thermal effect (effect of biological activity and vertical mixing) was adapted after the method proposed by Takahashi et al. (2002) as the following equations:

\[
\begin{align*}
\text{fCO}_2^{\text{therm}} &= \overline{f\text{CO}_2} \times \exp [0.0423 \cdot (\overline{\text{SST}} - \overline{\text{SST}})] \\
\text{fCO}_2^{\text{non-therm}} &= \text{fCO}_2 \times \exp [0.0423 \cdot (\overline{\text{SST}} - \overline{\text{SST}})] \\
\Delta f\text{CO}_2^{\text{therm}} &= f\text{CO}_2^{\text{therm}}_{\text{max}} - f\text{CO}_2^{\text{therm}}_{\text{min}} \\
\Delta f\text{CO}_2^{\text{non-therm}} &= f\text{CO}_2^{\text{non-therm}}_{\text{max}} - f\text{CO}_2^{\text{non-therm}}_{\text{min}}
\end{align*}
\]

where \( \overline{\text{SST}} \) is the surface seawater temperature in \( ^\circ\text{C} \), and the \( \overline{f\text{CO}_2} \) and \( \overline{\text{SST}} \) refer to the annual average of observed \( f\text{CO}_2 \) and SST values, respectively.

The dependence of \( f\text{CO}_2 \) variability in the UB on the thermal (\( f\text{CO}_2^{\text{therm}} \)) and non-thermal (\( f\text{CO}_2^{\text{non-therm}} \)) effects was separated by the equations above (Eq. 2 and 3). The results are shown in Figs. 5f and 5g. The \( f\text{CO}_2^{\text{therm}} \) followed the same pattern as the seasonal SST variation (Fig. 5a and 5f). The peak-to-peak amplitudes of the seasonal cycles of SST and \( f\text{CO}_2^{\text{therm}} \) (\( \Delta f\text{CO}_2^{\text{therm}} \), Eq. 4) were ~17 \( ^\circ\text{C} \) and 275 \( \mu \text{atm} \), respectively, which means that an 1 \( ^\circ\text{C} \) temperature change makes a 16 \( \mu \text{atm} \) change in \( f\text{CO}_2 \). Takahashi et al. (1993) suggested
the thermodynamic relationship between $pCO_2$ and temperature \((\partial pCO_2/\partial T)/pCO_2 = 0.0423 \, ^\circ C^{-1}\), our data showed almost close to it (0.0462 $^\circ C^{-1}$). However, the $\Delta fCO_2^{therm}$ was larger than that observed at Station “P” (100 $\mu$atm, Wong and Chan, 1991) and at BATS (150 $\mu$atm, Bates, 2001), which located at the comparable latitude as the UB. Larger seasonal variation of SST (>17°C) may have caused such a difference.

On the other hand, $fCO_2^{non-therm}$ reached its highest value during the cold season and its lowest value during the warm season. The peak-to-peak amplitude was 190 $\mu$atm, which was smaller than the value from the Ross Sea (260 $\mu$atm, Sweeney 2000) but much larger than the value from BATS (115 $\mu$atm, Bates 2001). This high $fCO_2^{non-therm}$ value in winter was due to (1) relatively low biological carbon uptake during the cold season, and (2) stronger vertical mixing that pumps up high-CO$_2$ subsurface water. The decrease in the $fCO_2^{non-therm}$ value of more than 100 $\mu$atm in spring was attributed to carbon fixation by the spring bloom (Fig. 5e and 5c). In summer, the value decreased because of weakening of vertical mixing caused by stratification (Fig. 5b and 5e).

The seasonal variation in $fCO_2$ can be explained by the sum of the thermal and non-thermal effects. The ratio between the thermal effect and the non-thermal effect was estimated to be almost equal to one ($\Delta fCO_2^{therm}/\Delta fCO_2^{non-therm} = 1.4$) in the UB, which suggested that the thermal effect was almost balanced with the non-thermal effect. A similar result (0.9) was obtained at Station “P” in the eastern subarctic Pacific Ocean (50° N, 145° W) during the period 1973–1978 (Wong and Chan 1991). On the other hand, the ratio differed significantly from that found for the BATS (2.7) (Bates 2001) or the Ross Sea (0.02) (Sweeney 2000) values (Table 2).

In summary, the contribution of temperature variation to the seasonality of $fCO_2$ was almost equivalent to the non-thermal effect in the UB. However, the relative contribution varied with the season (Fig. 5h). Non-thermal effect contributed to the surface $fCO_2$ drawdown in summer, while the surface $fCO_2$ elevation in winter. According to Sarmiento and Gruber (2006), $pCO_2$ in the North Pacific is not affected by one dominant factor among SST, biological activity, and vertical mixing but is affected by their combined effect. Their explanation about the controlling factors of $pCO_2$ in the North Pacific could be applied to similar features of the $fCO_2$ in the UB.
3.3 Long-term trend of $f$CO$_2$ and ocean acidification in the UB

Long-term trend of the $f$CO$_2$ in the UB is shown in Fig. 3. The long-term atmospheric $p$CO$_2$ variation observed at Gosan station (33° 17.4’ N, 126° 9.9’ E) in Jeju Island, WMO Gloabl Atmosphere Watch Station (Cho et al., 2005) is also shown in the figure for comparison with $f$CO$_2$ atm measured in the UB (Fig. 3b).

The $f$CO$_2$ atm in the UB coincided with $p$CO$_2$ at Gosan owing to the shorter turnover time of atmospheric CO$_2$ than that in the ocean. The trends of increasing $p$CO$_2$ at Gosan and $f$CO$_2$ in the UB were 1.9 ppm yr$^{-1}$ and 1.8 μatm yr$^{-1}$, respectively. These values were slightly larger than the global mean 1.5 ppm yr$^{-1}$ (IPCC, 2007).

Since the work of Inoue et al. (1995), numerous studies have focused on the rate of CO$_2$ increase based on monitoring and survey data. For the sake of comparing the long-term trend of the $f$CO$_2$ in the UB with other regions, previously published data covering approximately 30 different oceanic areas are listed in Table 3. The $f$CO$_2$ sea in the UB had been increasing gradually at a rate of 2.7 μatm yr$^{-1}$, which is in the middle of the increasing rates in the mid-latitude of the Northern Hemisphere (Fig. 6). Generally, the increasing rate in most areas is close to the global average (1.5 μatm yr$^{-1}$; IPCC 2007), but the rate in the middle latitudes of the Northern Hemisphere is higher. We could infer from this result that human activities might influence the rate of increase of CO$_2$ in surface seawater.

As surface water CO$_2$ has been increasing, the pH of the surface seawater has been decreasing, an effect called ocean acidification. The long-term trend of pH in the UB was estimated based on total alkalinity (TA) data from this study and $f$CO$_2$ sea. The pH values were calculated from TA and simulated $f$CO$_2$ sea by CO2SYS (Lewis and Wallace, 1998). The carbonate dissociation constants ($K_1$ and $K_2$) used in these calculations was those of Mehrbach et al. (1973) as refit by Dickson and Millero (1987). We assumed the TA of surface seawater to be constant at 2266 ± 17 μeq kg$^{-1}$, the average value of 60 measurements during the study period, because the seasonality and secular trends were not significant. These calculated pH values were in good agreement with the measured ones (Fig. 7b). As the surface $f$CO$_2$ increased, the pH value in the surface seawater of the UB, while fluctuating seasonally, decreased at the rate of 0.03 pH units decade$^{-1}$ since 1995 (Fig. 7). The pH in the surface ocean decreased by 0.1 pH units between 1750 and 1994, which was noted as an unprecedented decline by Sabine et al. (2004).
To compare $f$CO$_2$ increasing trend and pH decreasing trend in the UB with global trend, we also plotted time series of $f$CO$_2$ and pH from Station ALOHA data during the same period. Since 1995, the $p$CO$_2$ at Station ALOHA has increased at a rate of $\sim$1.6 µatm yr$^{-1}$ and mixed layer pH has declined by 0.02 pH units per decade (Fig. 7). IPCC (2007) reported that the rate of decrease of pH was estimated at about 0.02 pH units decade$^{-1}$ based on station data at HOT, BATS, and ESTOC since 1980. Compared with the global trend, surface seawater of the UB has being acidified faster.

Under the assumption of constant TA and sea surface temperature, 10% increase of $f$CO$_2$ in the UB (i.e. 26.6 µatm increase in a decade) may reduce pH by 0.027 pH units which contributes about 87% of pH decrease in the UB during the last decade. A seawater temperature rise of 1°C may also decrease pH by 0.01 pH units at a pressure of 1 atm (Gieskes, 1969). The sea surface temperature in the EJS increased by 0.2 – 0.7 °C during the last decade (Kim et al., 2007; Yeh et al., 2010), which is a much faster warming than the global average (0.13°C decade$^{-1}$; Rayner et al., 2006). This warming contributed to a pH decrease of 0.002 – 0.007 pH units which was equivalent to 7 – 23% of the pH decline in the UB during the last decade. Therefore, the ocean acidification in the UB was mainly driven by the $f$CO$_2$ increase, while the warming effect was relatively small.

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Table 1. Information for cruises in this study. SST, fCO$_2$ atm, fCO$_2$ sea, ΔfCO$_2$, total alkalinity (TA), and pH are reported as averages and standard deviations. The average values are arithmetic mean of 1 minute or 2 minute averaged values in the cruise. The number of data values are listed in parentheses.

<table>
<thead>
<tr>
<th>Cruise Name</th>
<th>Observation Period</th>
<th>Research Vessel</th>
<th>SST(°C)</th>
<th>SSS</th>
<th>fCO$_2$ atm (μatm)</th>
<th>fCO$_2$ sea (μatm)</th>
<th>ΔfCO$_2$ (μatm)</th>
<th>TA (μeq kg$^{-1}$)</th>
<th>pH</th>
<th>Source</th>
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<tr>
<td>9508</td>
<td>6 Aug -7 Aug 1995</td>
<td>R/V Professor Khromov</td>
<td>24.1±1.5 (40)</td>
<td>32.6±0.3 (40)</td>
<td>353.0±3.1 (40)</td>
<td>365.4±13.6 (40)</td>
<td>12.4±12.8 (40)</td>
<td>N/A</td>
<td>N/A</td>
<td>Oh et al., 1999</td>
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<tr>
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<td>R/V Parvel Gordienko</td>
<td>9.2±1.2 (256)</td>
<td>34.3±0.1 (256)</td>
<td>362.9±0.4 (256)</td>
<td>311.2±14.3 (256)</td>
<td>-51.7±14.4 (256)</td>
<td>N/A</td>
<td>N/A</td>
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<tr>
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<td>33.4±0.7 (233)</td>
<td>346.8±2.6 (233)</td>
<td>359.7±36.3 (233)</td>
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<td>This study</td>
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<td>12.8±1.4 (3857)</td>
<td>34.3±0.1 (3857)</td>
<td>375.9±8.6 (712)</td>
<td>280.5±41.1 (1141)</td>
<td>-92.8±41.2 (1142)</td>
<td>N/A</td>
<td>N/A</td>
<td>This study</td>
</tr>
<tr>
<td>0306</td>
<td>9 Jun - 14 Jun 2003</td>
<td>R/V Tamgu-5</td>
<td>19.5±0.4 (2233)</td>
<td>33.6±0.4 (2233)</td>
<td>366.9±2.3 (2233)</td>
<td>353.7±19.2 (1319)</td>
<td>-29.1±18.6 (1319)</td>
<td>2256±21 (29)</td>
<td>8.0±0.03 (29)</td>
<td>This study</td>
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<tr>
<td>0312</td>
<td>12 Dec - 22 Dec 2003</td>
<td>R/V Tamgu-5</td>
<td>16.4±0.5 (1392)</td>
<td>33.9±0.1 (1392)</td>
<td>379.7±0.9 (120)</td>
<td>390.1±15.3 (401)</td>
<td>-3.9±14.7 (401)</td>
<td>N/A</td>
<td>N/A</td>
<td>This study</td>
</tr>
<tr>
<td>0405</td>
<td>6 May - 19 May 2004</td>
<td>R/V Akademik Labrantiev</td>
<td>17.8±1.8 (5153)</td>
<td>34.3±0.2 (5153)</td>
<td>376.6±3.3 (846)</td>
<td>354±23.6 (3113)</td>
<td>-50.1±22.7 (3113)</td>
<td>228±8 (8)</td>
<td>N/A</td>
<td>This study</td>
</tr>
<tr>
<td>0406</td>
<td>10 Jun - 11 Jun 2004</td>
<td>R/V Tamgu-5</td>
<td>19.8±0.2 (334)</td>
<td>34.2±0.2 (334)</td>
<td>368.6±0.3 (80)</td>
<td>336.5±7 (194)</td>
<td>-50.7±6.1 (194)</td>
<td>N/A</td>
<td>8.0±0.02 (21)</td>
<td>This study</td>
</tr>
<tr>
<td>0409</td>
<td>14 Sep -15 Sep 2004</td>
<td>R/V Tamgu-1</td>
<td>26.2±2.4 (806)</td>
<td>32.6±2.4 (806)</td>
<td>368.8±3.9 (64)</td>
<td>348.8±7.9 (245)</td>
<td>-26.6±8.4 (245)</td>
<td>N/A</td>
<td>N/A</td>
<td>This study</td>
</tr>
<tr>
<td>0410</td>
<td>5 Oct - 29 Oct 2004</td>
<td>R/V Tamgu-5</td>
<td>23.0±1.2 (4362)</td>
<td>33.4±0.2 (4362)</td>
<td>371.5±2.9 (563)</td>
<td>379.3±17.9 (2673)</td>
<td>-30.6±16.4 (2673)</td>
<td>226±8 (8)</td>
<td>8.0±0.03 (8)</td>
<td>This study</td>
</tr>
<tr>
<td>0811</td>
<td>1 Nov – 7 Nov 2008</td>
<td>R/V Eardo</td>
<td>19.8±1.1 (297)</td>
<td>33.3±0.1 (297)</td>
<td>389.3±8.0 (297)</td>
<td>359.5±12.2 (297)</td>
<td>-29.8±14 (297)</td>
<td>N/A</td>
<td>N/A</td>
<td>This study</td>
</tr>
<tr>
<td>0907</td>
<td>9 Jul – 10 Jul 2009</td>
<td>R/V Akademik Labrantiev</td>
<td>21.2±0.7 (546)</td>
<td>33.7±0.1 (546)</td>
<td>375.8±4.1 (546)</td>
<td>397.5±22.3 (546)</td>
<td>21.7±21.5 (546)</td>
<td>N/A</td>
<td>N/A</td>
<td>This study</td>
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<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td><strong>18.5±4.23</strong></td>
<td><strong>33.9±0.54</strong></td>
<td><strong>370.5±8.7</strong></td>
<td><strong>350.9±41.8</strong></td>
<td><strong>-41.4±36.5</strong></td>
<td><strong>2266±17</strong></td>
<td><strong>8.0±0.02</strong></td>
<td>This study</td>
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</table>
Table 2. Comparison of the contribution of thermal and non-thermal effects on the $\delta$CO$_2$ of surface seawater in various regions.

<table>
<thead>
<tr>
<th>Station</th>
<th>Thermal effect ($\mu$atm)</th>
<th>Non-thermal effect ($\mu$atm)</th>
<th>Ratio (Therm/non-Therm)</th>
<th>location</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>UB</td>
<td>275</td>
<td>190</td>
<td>1.4</td>
<td>36-38 °N, 130-133 °E</td>
<td>This Study</td>
</tr>
<tr>
<td>BATS</td>
<td>150</td>
<td>55</td>
<td>2.7</td>
<td>32 ° 50' N, 64 ° 10' W</td>
<td>Bates, 2001; Takahashi et al., 2002</td>
</tr>
<tr>
<td>Ross Sea</td>
<td>5</td>
<td>260</td>
<td>0.02</td>
<td>76 ° 30' S, 169 °E- 177 ° W</td>
<td>Sweeney, 2000; Takahashi et al., 2002</td>
</tr>
<tr>
<td>Station “P”</td>
<td>100</td>
<td>115</td>
<td>0.9</td>
<td>50 ° N, 145 ° W</td>
<td>Wong and Chan, 1991; Takahashi et al., 2002</td>
</tr>
</tbody>
</table>
Table 3. Rate of increase of surface seawater CO₂ at various regions of the world ocean.

<table>
<thead>
<tr>
<th>Region</th>
<th>Increasing Rate (μatm yr⁻¹)</th>
<th>Duration</th>
<th>Area</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Pacific</td>
<td>1.3±0.2</td>
<td>1970-2004</td>
<td>Whole Pacific</td>
<td>Takahashi et al., 2006</td>
</tr>
<tr>
<td>Central Equatorial Pacific</td>
<td>1.8±0.7</td>
<td>1979 -2001</td>
<td>5°N – 5°S</td>
<td>Takahashi et al., 2003</td>
</tr>
<tr>
<td>Western Equatorial Pacific</td>
<td>3.4±0.4</td>
<td>1979 -2001</td>
<td>5°N – 5°S</td>
<td>Takahashi et al., 2003</td>
</tr>
<tr>
<td>Western Equatorial Pacific</td>
<td>1.5±0.2</td>
<td>1985-2004</td>
<td>5°S – 5°N, 144°E – 160°W</td>
<td>Ishii et al., 2009</td>
</tr>
<tr>
<td>Western North Pacific</td>
<td>1.8±0.6</td>
<td>1984-1993</td>
<td>15°N - 35°N, 132°E - 142°E</td>
<td>Inoue et al., 1995</td>
</tr>
<tr>
<td>Western North Pacific</td>
<td>0.5±0.7</td>
<td>1984-1993</td>
<td>3°N - 14°N, 132°E – 142°E</td>
<td>Inoue et al., 1995</td>
</tr>
<tr>
<td>Western North Pacific</td>
<td>2.1</td>
<td>1995-2007</td>
<td>35°N, 147.5°E</td>
<td>Nojiri and Tsumori, 2007</td>
</tr>
<tr>
<td>Subtropical North Pacific</td>
<td>1.8±0.6</td>
<td>1996-2005</td>
<td>30°N - 42°N, 120°E – 105°W</td>
<td>Lenton et al., 2012</td>
</tr>
<tr>
<td>Central North Pacific</td>
<td>0.8</td>
<td>1995-2006</td>
<td>40°N, 175°E</td>
<td>Nojiri and Tsumori, 2007</td>
</tr>
<tr>
<td>Eastern North Pacific</td>
<td>0.9</td>
<td>1995-2006</td>
<td>35°N, 140°W</td>
<td>Nojiri and Tsumori, 2007</td>
</tr>
<tr>
<td>Western Subarctic North Pacific</td>
<td>0.6</td>
<td>1995-2006</td>
<td>45°N, 155°E</td>
<td>Nojiri and Tsumori, 2007</td>
</tr>
<tr>
<td>Western Subarctic North Pacific</td>
<td>1.6±1.7</td>
<td>1995-2003</td>
<td>42°S – 50°N, 150°E – 170°E</td>
<td>Lenton et al., 2012</td>
</tr>
<tr>
<td>North Atlantic Subpolar Gyre</td>
<td>1.8</td>
<td>1982-1998</td>
<td>50°N – 70°S, 80°W – 10°W</td>
<td>Lefèvre et al., 2004</td>
</tr>
<tr>
<td>South Indian Ocean</td>
<td>1.1</td>
<td></td>
<td>20°S</td>
<td>Inoue and Ishii, 2005</td>
</tr>
<tr>
<td>South Indian Ocean</td>
<td>1.4</td>
<td></td>
<td>40°S</td>
<td>Inoue and Ishii, 2005</td>
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<tr>
<td>Southern Ocean</td>
<td>2.3±0.2</td>
<td>1995-2008</td>
<td>42°S – 62°S, Circumpol</td>
<td>Lenton et al., 2012</td>
</tr>
<tr>
<td>South of Australia (Sub-Antarctic Zone)</td>
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<td>50°S, 140°E - 160°E</td>
<td>Inoue and Ishii, 2005</td>
</tr>
<tr>
<td>South of Australia (Polar Frontal Zone)</td>
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<td>55°S, 140°E - 160°E</td>
<td>Inoue and Ishii, 2005</td>
</tr>
<tr>
<td>South of Australia (Polar Zone)</td>
<td>1.8</td>
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<td>58°S, 140°E - 160°E</td>
<td>Inoue and Ishii, 2005</td>
</tr>
<tr>
<td>ALOHA</td>
<td>2.5±0.3</td>
<td>1989-2001</td>
<td>22.7°N, 158°W</td>
<td>Dore et al., 2003</td>
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<tr>
<td>ALOHA</td>
<td>3.2±0.4</td>
<td>1997-2002</td>
<td>22.7°N, 158°W</td>
<td>Keeling et al., 2004</td>
</tr>
<tr>
<td>ALOHA</td>
<td>1.4±0.2</td>
<td>1988-1996</td>
<td>22.7°N, 158°W</td>
<td>Keeling et al., 2004</td>
</tr>
<tr>
<td>SEATS</td>
<td>4.2±3.2</td>
<td>1995-2004</td>
<td>18°N, 116°E</td>
<td>Tseng et al., 2007</td>
</tr>
<tr>
<td>ESTOC site</td>
<td>1.55</td>
<td>1995-2004</td>
<td>29.16°N, 15.5°W</td>
<td>Santana-Casino et al., 2007</td>
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<tr>
<td>BATS</td>
<td>1.67±0.28</td>
<td>1983-2005</td>
<td>31.7°N, 64.5°W</td>
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<tr>
<td>UB</td>
<td>2.7</td>
<td>1995-2004</td>
<td>36°N - 38°N, 130°E - 133°E</td>
<td>This study</td>
</tr>
<tr>
<td>Global Mean</td>
<td>1.5</td>
<td></td>
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<td>IPCC, 2007</td>
</tr>
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</table>
Figure 1. Maps showing the tracks of the cruises conducted between 1995 and 2009 for this study.
Figure 2. The secular variations in $f\text{CO}_2^{\text{sea}}$ (filled circles) and $f\text{CO}_2^{\text{atm}}$ (open diamonds) in the Ulleung Basin, East/Japan Sea, from 1995 to 2009. Error bars represent one standard deviation from the mean value.
Figure 3. Long-term trend of $f$CO$_2$ at the Ulleung Basin from 1995 to 2009. (a) $f$CO$_2$$_{sea}$ (filled circles) of surface seawater of the Ulleung Basin, (b) $f$CO$_2$$_{atm}$ (filled diamonds) of overlying atmosphere of the Ulleung Basin. Atmospheric $p$CO$_2$ data, measured at Gosan, Jeju Island, Korea (gray dots), are also shown for comparison with $f$CO$_2$$_{atm}$. The gray curves represent $f$CO$_2$ fitted from a harmonic function analysis by Eq. (1).
Figure 4. (a) The secular variations in $\Delta f_{CO_2}$ and (b) monthly variation of $\Delta f_{CO_2}$ in the Ulleung Basin, East/Japan Sea, from 1995 to 2009. Error bars represent one standard deviation from the mean value.
Figure 5. Monthly variations in the (a) sea surface temperature (SST), (b) mixed layer depth (MLD), (c) chlorophyll-\(a\) in the surface water, (d) \(fCO_2^{\text{therm}}\), (e) \(fCO_2^{\text{non-therm}}\), and (f) ratio of the thermal to non-thermal effects \((fCO_2^{\text{therm}}/fCO_2^{\text{non-therm}})\) in the UB. The MLD was based on the climatology by de Boyer-Montégut et al. (2004). The chlorophyll-\(a\) was based on the SeaWiFS data between 1998 to 2007.
Figure 6. A plot of the rate of increase of surface seawater CO$_2$ versus latitude. Dashed line represents the global average of surface seawater increasing rate (1.5 µatm yr$^{-1}$).
Figure 7. Secular variation of (a) $f$CO$_2$ ($\mu$atm) (black filled circles and fitting line), and (b) pH (black diamonds and fitting line) of the surface water in the UB. The time-series $p$CO$_2$ ($\mu$atm) (gray open circles) and pH (gray open squares) at Station ALOHA in the subtropical North Pacific Ocean are also shown for comparison. The $p$CO$_2$ and pH data at Station ALOHA are from D. Karl, University of Hawaii, http://hahana.soest.hawaii.edu., and are updated from Doney et al. (2009) and Dore et al. (2003).