Ocean acidification from 1997 to 2011 in the subarctic western North Pacific Ocean

M. Wakita1,2, S. Watanabe1, M. Honda2, A. Nagano2, K. Kimoto2, K. Matsumoto1,2, M. Kitamura3, K. Sasaki1,2, H. Kawakami1,2, T. Fujiki2, K. Sasaoka2, Y. Nakano4, and A. Murata2

1Mutsu Institute for Oceanography, Japan Agency for Marine-Earth Science and Technology, Mutsu, Japan
2Research Institute for Global Change, Japan Agency for Marine-Earth Science and Technology, Yokosuka, Japan
3Institute of Biogeosciences, Japan Agency for Marine-Earth Science and Technology, Yokosuka, Japan
4Marine Technology and Engineering Center, Japan Agency for Marine-Earth Science and Technology, Yokosuka, Japan

Correspondence to: M. Wakita (mwakita@jamstec.go.jp)

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Abstract. Rising atmospheric CO2 contents have led to greater CO2 uptake by the oceans, lowering both pH due to increasing hydrogen ions and CaCO3 saturation states due to declining carbonate ion (CO3^-2). Here we used previously compiled data sets and new data collected in 2010 and 2011 to investigate ocean acidification of the North Pacific western subarctic gyre. In winter, the western subarctic gyre is a source of CO2 to the atmosphere because of convective mixing of deep waters rich in dissolved inorganic carbon (DIC). We calculated pH in winter mixed layer from DIC and total alkalinity (TA), and found that it decreased at the rate of -0.0001 ± 0.0004 yr^-1 from 1997 to 2011. This decrease rate is slower than that expected under the condition of seawater/atmosphere equilibration, and it is also slower than the rate in the subtropical regions (-0.002 yr^-1). The slow rate is caused by a reduction of CO2 uptake in winter due to an increase in TA. Below the mixed layer, the calcite saturation horizon (~185 m depth) shoaled at the rate of 2.9 ± 0.9 m yr^-1 as the result of the declining CO3^-2 concentration (-0.03 ± 0.01 mmol kg^-1 yr^-1). Between 200 m and 300 m depth, pH decline during the study period (-0.0051 ± 0.0010 yr^-1) was larger than ever reported in the open North Pacific. This enhanced acidification rate below the calcite saturation horizon reflected not only the uptake of anthropogenic CO2 but also the increase in the decomposition of organic matter evaluated from the increase in AOU, which suggests that the dissolution of CaCO3 particles increased.

1 Introduction

Globally, anthropogenic CO2 was taken up by the oceans at a rate of 2.2 ± 0.4 Pg C yr^-1 during the 1990s (Bindoff et al., 2007). This CO2 uptake by the oceans has increased the hydrogen ion (H+) concentration (i.e., lowered the pH) and lowered the CaCO3 saturation state (Ω), by decreasing the carbonate ion (CO3^-2) concentration, thereby leading to bicarbonate ion (HCO3^-) formation. These changes in the carbonate system affect marine organisms and ecosystems throughout the world’s oceans (Doney et al., 2009).

Ocean acidification of surface and subsurface waters of the North Pacific Ocean has been clearly documented in time series and repeat hydrography data (direct basin-wide observations) over the past two decades (e.g., Dore et al., 2009; Byrne et al., 2010; Midorikawa et al., 2010; Ishii et al., 2011; Feely et al., 2004; Feely et al., 2012; Murata and Saito, 2012). The observed pH changes in the surface ocean are consistent with those predicted based on equilibration of atmospheric CO2 with the seawater (about -0.002 yr^-1) (Dore et al., 2009; Byrne et al., 2010; Midorikawa et al., 2010; Ishii et al., 2011). In subsurface water, pH decreases (-0.003 yr^-1 at Station ALOHA (22.75° N; 158° W; Dore et al. (2009) and 0.004 yr^-1 in North Pacific Intermediate Water; Byrne et al. (2010)) have been enhanced by the accumulation of anthropogenic CO2 and by natural variability related to temporal changes in physical and biogeochemical processes such as ocean ventilation, and remineralization of organic matter related to apparent oxygen utilization (AOU). The downward
transport of anthropogenic CO$_2$ taken up by the oceans since the preindustrial era has caused shoaling of the CaCO$_3$ saturation horizons of both aragonite and calcite in the North Pacific (Feely and Chen, 1982; Feely et al., 2004, 2012; Murata and Saito, 2012). These results are caused by an increase of H$^+$ (i.e., a decrease of pH) and a concurrent decrease of CO$_2$ concentration, and will impact many marine calcifying species in surface and subsurface water of North Pacific (e.g., coccolithophores, foraminifera, and pteropods). Furthermore, the observed increase in total alkalinity (TA) at the depth of the aragonite saturation horizon between 1970 and 1990 is consistent with the calculated increase in CaCO$_3$ dissolution caused by the shoaling of the horizon (Sarma et al., 2002), although the uncertainty is large (Bindoff et al., 2007).

Projections of the CaCO$_3$ saturation horizon of aragonite based on the Intergovernmental Panel on Climate Change (IPCC) IS92a scenario (an atmospheric CO$_2$ concentration of 788 ppmv in 2100) for future emissions of anthropogenic CO$_2$ indicate that the surface mixed layer (0–100 m) in the Southern Ocean, and the subarctic Pacific Ocean will become undersaturated with respect to aragonite around 2020–2040 (Orr et al., 2005; Guinotte et al., 2006). For this reason, seawater at the high latitudes has a high Revelle factor, which is a low CO$_2$ buffering capacity in seawater, and is characterized by low concentrations of CO$_2$ and shallow of CaCO$_3$ saturation horizon (Takahashi et al., 2002; Feely et al., 2004). Thus, even if a smaller change in Ω accompanies future increases in atmospheric CO$_2$, the surface waters in these regions will be the first to switch from being supersaturated to being undersaturated with respect to CaCO$_3$. In particular, models project that the first region to become undersaturated will be the western subarctic North Pacific (Fig. 1) during winter (Orr et al., 2005; Guinotte et al., 2006), because winter surface waters in this region have lower Ω content and shallower CaCO$_3$ saturation horizon (Fig. 2) than the open Pacific Ocean and Southern Ocean (Feely et al., 2004; Feely et al., 2012). The lower Ω in the winter is caused by the convective mixing of deep waters rich in dissolved inorganic carbon (DIC), accompanying with a strong CO$_2$ source (e.g., Tsurushima et al., 2002; Wakita et al., 2010a) (Fig. 2). These results mean that in this region, ocean acidification in winter is affected not only by increases in atmospheric CO$_2$ but also by decadal variations of CO$_2$ emissions. Therefore, assessment of the present progression of acidification in winter in the western subarctic gyre of the North Pacific from field observations is an urgent task.

In this study, we are aimed at clarifying progression of ocean acidification in winter in the western subarctic gyre by examining the temporal changes of pH and CaCO$_3$ saturation horizon, which are indicators of ocean acidification, and related chemical properties (dissolved inorganic carbon (DIC), TA, and oceanic CO$_2$) below the winter mixed layer at two time-series stations (K2 and KNOT) during the period 1997–2011 (Fig. 1).

2 Data and analyses

From January 2010 to July 2011, we conducted hydrographic observations at stations K2 and KNOT during five cruises (MR10-01, January to February 2010; MR10-06, October 2010; MR11-02, February to March 2011; MR11-03, April 2011, and MR11-05, July 2011) of the R/V Mirai of the Japan Agency for Marine-Earth Science and Technology. These observations comprised 20 CTD casts at K2, and in four CTD casts at KNOT. DIC and TA were measured by using coulometric and potentiometrical techniques, respectively. Those values were calibrated against certified reference material provided by A. G. Dickson (Scripps Institution of Oceanography). The precision of both DIC and TA was ±0.1 %. Dissolved oxygen (DO) and nutrients (silicate, phosphate, and nitrate) concentrations were measured with an automatic photometric titrator and a continuous flow analyzer, respectively. Data sets collected at K2 and KNOT from 2010 to 2011 will be opened to publish on the JAMSTEC data web site (http://ebcrpa.jamstec.go.jp/k2s1/en/index.html) and the Carbon Dioxide Information and Analysis Center web site (http://cdiac.ornl.gov/oceans/Moorings/K2.html). We also merged compiled data sets from KNOT and K2 for the period 1997–2008, in which the systematic errors were corrected (Wakita et al., 2010b, c). In addition, we used oceanic physical and chemical data collected at KNOT and K2 during WOCE–P1 (2007) (Fukasawa et al., 2008).

K2 and KNOT are both located in the western subarctic gyre (Fig. 1). We obtained a decadal time series by combining data from the two stations, because the duration of sampling at each individual station data was not sufficient.
Fig. 2. Seasonal variations of (a) the maximum mixed-layer depth (MLD), (b) sea surface temperature (SST), (c) oceanic and atmospheric $\mathrm{CO}_2$, (d) DIC, (e) TA, (f) phosphate, (g) pH (total scale) at the in situ temperature ($\mathrm{pH}_{\text{in situ}}$), and (h) CaCO$_3$ saturation states ($\Omega$) with respect to aragonite and calcite in the surface mixed layer at KNOT (blue circles) and K2 (red circles). These figures were plotted using all data from 1997 to 2011 in order to examine typical seasonal variations and for comparison with the climatological monthly means of MIxed Layer data set of Argo, Grid Point Value (MILA GPV) (Hosoda et al., 2010) (a, b), data from Station ALOHA (Dore et al., 2010) (b–g), and Takahashi et al. (2009) (c). Values of oceanic $\mathrm{CO}_2$ (c), $\mathrm{pH}_{\text{in situ}}$ (g) and $\Omega$ (h) were calculated from TA and DIC. The density criterion in the surface mixed layer was smaller than 0.125 kg m$^{-3}$ (de Boyer Montégut et al., 2004).

Typically, in this region the minimum temperature ($T_{\text{min}}$) in the water column is associated with the remnant of the mixed layer water in the preceding winter and occurs at about 26.5$\sigma_0$ ($\sim$ 100 m), and the maximum temperature occurs at about 27.1$\sigma_0$ ($\sim$ 370 m) (e.g., Ueno and Yasuda, 2000; Osa-fune and Yasuda, 2006). Each year, the surface mixed layer reached its maximum depth from mid-March to early April (Fig. 2a) and the coldest mixed-layer temperatures were observed in early April (Fig. 2b). Because spring to fall surface mixed layer temperatures did not influence $T_{\text{min}}$ (Wakita et al., 2010a), we identify the $T_{\text{min}}$ layer as the remnant of the winter (early April) mixed-layer water. However, station
KNOT is just north of the subarctic front (Fig. 1), so occasionally no $T_{\min}$ water is observed because of the northward migration of subtropical water (Tsurushima et al., 2002). Because this migrated subtropical water enters the south edge of western subarctic gyre and passes eastward (Ueno and Yasuda, 2000), we did not use observation data if no $T_{\min}$ layer could be identified. This indicates the combined K2 and KNOT data in this study does not include the subtropical water and is not obviously different in hydrography.

DIC, TA, phosphate, silicate and AOU in the winter mixed layer (i.e., DIC$_{\text{win}}$, TA$_{\text{win}}$, PO$_4$$_{\text{win}}$, Si$_{\text{win}}$, AOU$_{\text{win}}$) are obtained from in the corresponding values in the $T_{\min}$ layer (DIC$_{T_{\min}}$, TA$_{T_{\min}}$, PO$_4$$_{T_{\min}}$, Si$_{T_{\min}}$ and AOU$_{T_{\min}}$) following Wakita et al. (2010a). DIC$_{T_{\min}}$, AOU$_{T_{\min}}$, PO$_4$$_{T_{\min}}$, and Si$_{T_{\min}}$ varied seasonally, reaching minima in winter, but TA$_{T_{\min}}$ showed no distinct seasonal variation (Wakita et al., 2010a). In spring, observed values of DIC$_{T_{\min}}$, AOU$_{T_{\min}}$, PO$_4$$_{T_{\min}}$, and Si$_{T_{\min}}$ increased compared with those of the previous winter because of the decomposition of organic matter. We calculated AOU by subtracting the observed DO concentration from the saturated concentration calculated from temperature and salinity using the equation of Weiss (1970). We assumed that DO in the winter mixed layer was homogeneously saturated (i.e., AOU = 0) because of strong vertical mixing and air–sea exchange. We calculated DIC$_{\text{win}}$, PO$_4$$_{\text{win}}$, and Si$_{\text{win}}$ from observed DIC$_{T_{\min}}$, PO$_4$$_{T_{\min}}$, and Si$_{T_{\min}}$ and stoichiometric ratios of decomposition with the following equations:

\[
\begin{align*}
\text{DIC}_{\text{win}} &= \text{DIC}_{T_{\min}} - (C/ -O_2) \times \text{AOU}_{T_{\min}} \\
\text{PO}_4_{\text{win}} &= \text{PO}_4_{T_{\min}} - (P/ -O_2) \times \text{AOU}_{T_{\min}} \\
\text{Si}_{\text{win}} &= \text{Si}_{T_{\min}} - (Si/ -O_2) \times \text{AOU}_{T_{\min}},
\end{align*}
\]

where $(C/ -O_2)$ (117/170) and $(P/ -O_2)$ (1/170) are the stoichiometric ratios of carbon and phosphorus to oxygen during the decomposition of organic matter (Anderson and Sarmiento, 1994). We used $(Si/ -O_2)$ of 0.18 because Si$_{T_{\min}}$ was positively correlated with AOU$_{T_{\min}}$ ($r = 0.76$, $p < 0.001$).

After the values of $T_{\min}$ (depth, temperature, salinity, and $\sigma_T$) were determined from continuous CTD data (1 db resolution), we obtained DO, DIC, TA, and nutrients concentrations at the isopycnal surface where $T_{\min}$ occurred by linear interpolation of discrete bottle-sampling data. Note that the values of depth, salinity and $\sigma_T$ in the $T_{\min}$ layer from continuous CTD data are not necessarily identical to those from discrete bottle sampling. For the isopycnal analysis, the values of DO, DIC, TA, and nutrients on each isopycnal surface from 26.7$\sigma_T$ to 27.0$\sigma_T$ were also obtained by linear interpolation of discrete bottle sampling data.

Using CO2SYS software (Pierrot et al., 2006), we calculated the mixing ratio of CO$_2$ by volume in dry air ($x$CO$_2$), pH (total scale) at the in situ temperature ($pH_{\text{in situ}}$) and at 25 °C ($pH_{25}$), the free hydrogen ion concentration ($[H^+]_F$), the carbonate ion concentration ($CO_3^{2-}$), and $\Omega$ from measured DIC, TA, phosphate, and silicate values. The carbonate dissociation constants required for the calculation are Mehrbach et al. (1973) as refitted by Dickson and Millero (1987), by using potential temperature, salinity and 0 db pressure in the winter mixed layer ($T_{\min}$ layer), and the in situ temperature, salinity and in situ pressure in subsurface waters. We also calculated $\Omega$ with respect to the two minerals forms of CaCO$_3$, aragonite ($\Omega_{\text{aragonite}}$) and calcite ($\Omega_{\text{calcite}}$), as the ion product of calcium ion (Ca$^{2+}$) and CO$_3^{2-}$ ions:

\[
\Omega = [\text{Ca}^{2+}][\text{CO}_3^{2-}] / K'_{\text{sp}}.
\]

where the square brackets indicate the concentrations of the enclosed species, and $K'_{\text{sp}}$ is the thermodynamic solubility product constant for aragonite or calcite (Mucci, 1983). We estimated [Ca$^{2+}$] by assuming the following linear relationship with salinity (S): $[\text{Ca}^{2+}] = 0.01028 \times S/35$ (Millero, 1982). Applying this [Ca$^{2+}$] equation to calculate the CaCO$_3$ saturation horizon will be reasonable, because the notable carbonate-forming biota such as coccolithophore and planktonic foraminifera; pteropods in the western subarctic gyre are living in the surface water (0–100 m) (Hattori et al., 2004, Sagawa et al., 2012, Fukuji et al., 2009, Steinberg et al., 2008), where it was shallower than the CaCO$_3$ saturation horizon of aragonite (∼120 m) (Feely et al., 2004).

3 Results and Discussion

3.1 Acidification in the winter mixed layer

During the study period, pH$_{\text{in situ}}^{25}$ and pH$_T^{25}$ in the winter mixed layer significantly decreased at a rate of $-0.0011 \pm 0.0004$ yr$^{-1}$ ($p < 0.01$) and $-0.0010 \pm 0.0004$ yr$^{-1}$ ($p < 0.05$), respectively (Fig. 3), whereas $\Omega_{\text{aragonite}}$ $\Omega_{\text{calcite}}$ and CO$_3^{2-}$ did not decrease significantly ($p > 0.08$) (not shown). We estimated pH$_{\text{in situ}}^{25}$, $\Omega_{\text{aragonite}}$, $\Omega_{\text{calcite}}$, and xCO$_2$ in the winter mixed layer from DIC, TA, phosphate and silicate as describe in Sect. 2.

In the winter mixed layer, pH decreased more slowly than predicted from oceanic equilibration with the increasing atmospheric CO$_2$ ($-0.002$ pH$_{\text{in situ}}$ yr$^{-1}$), when it was calculated by using the increase in atmospheric CO$_2$ (2.1 ppm yr$^{-1}$) in late winter (the beginning of April) from 1997 to 2011 at 44.4°N (Conway et al., 2012) and constant TA$_{\text{win}}$. In addition, the pH decreasing rate was slower than the rates that determined in the central North Pacific near Hawaii ($-0.0019 \pm 0.0002$ pH$_{\text{in situ}}$ yr$^{-1}$; Dore et al., 2009), the subtropical western North Pacific along 137°E in winter ($-0.0015 \pm 0.0002$ pH$_{\text{in situ}}$ yr$^{-1}$ to $-0.0021 \pm 0.0002$ pH$_{\text{in situ}}$ yr$^{-1}$; Midoriwaka et al., 2010), off the south coast of Honshu, Japan ($-0.0020 \pm 0.0007$ pH$_{\text{in situ}}$ yr$^{-1}$; Ishii et al., 2011) and along 152°W between Hawaii and Alaska ($-0.0017$ pH$_{\text{in situ}}$ yr$^{-1}$; Byrne et al., 2010).

Because the western subarctic gyre is a source of CO$_2$ to the atmosphere in winter, owing to strong vertical mixing of
If TA in seawater increases over time, then the increase of oceanic xCO2 in winter (red line, \(0.9\pm0.04 \text{ppm yr}^{-1}, p<0.01\)) is significantly higher than
that of oceanic xCO2 in winter (green line, \(2.1\pm0.04 \text{ppm yr}^{-1}, p<0.005\));
ta in winter (blue line, \(0.5\pm0.2 \mu\text{mol kg}^{-1} \text{yr}^{-1}, p<0.01\)); and DICwin (red line, \(0.9\pm0.2 \mu\text{mol kg}^{-1} \text{yr}^{-1}, p<0.001\)).
Regression lines shown for the theoretical \(pH_{\text{in situ}}^{\text{calcite}=1}\) (blue dashed line, \(-0.0026 \text{yr}^{-1}\)) and \(xCO2\) in the ocean (red dashed line, \(2.6 \text{ppm yr}^{-1}\)) were calculated by using increasing values of DIC and constant TA (2240 \(\mu\text{mol kg}^{-1}\)).

In addition to the increase in DICwin and TAwin, PO4\(_{\text{win}}\) and Si\(_{\text{win}}\) also significantly increased during the period 1997–2011 (0.012\(\pm0.002 \mu\text{mol kg}^{-1} \text{yr}^{-1}, p<0.001\), and 0.28\(\pm0.09 \mu\text{mol kg}^{-1} \text{yr}^{-1}, p<0.05\), respectively), whereas the density of the winter mixed layer (\(T_{\text{min}}\) layer) significantly decreased (\(-0.003 \pm0.002 \text{kg m}^{-3} \text{yr}^{-1}, p<0.05\)).

These results differ from those of Ono et al. (2001, 2002), who reported linear decreasing trends in physical and chemical properties such as salinity, and phosphate in the winter mixed layer in the Oyashio region and the subarctic western North Pacific from 1968 to 1998 as a result of occurrence of surface stratification. More accurate data and longer time series are required to determine the reason for this discrepancy.
and calcite (Ω(calcite)) state of seawater with respect to aragonite (Ω(aragonite)) in the atmosphere (−0.002 yr−1). Similarly, the rate of [H+]F increase in the in the 26.7–27.0σθ layer (1.0 × 10−10 to 2.9 × 10−10 mol kg−1 yr−1) was faster than the acidity rate expected from equilibration with the atmosphere (0.4 × 10−10 mol kg−1 yr−1) (Table 1). Acidity ([H+]F) is on a logarithmic scale as pH (−log10[H+]F). Their rates of pH decline at various depths actually represented different rates of [H+]F accumulation. Decadal change of maximum pH decline in the subsurface water (−0.05) corresponds to an approximately 10% increase in [H+]F. The elevated acidification rate at 26.9σθ (Table 1) is higher than the previous observed rate in the open North Pacific (at 250 m depth at Station ALOHA, −0.003 pH(θ) in situ yr−1; Dore et al., 2009, and in the upper 500 m along 152° W between Hawaii and Alaska, −0.004 pH(θ) in situ yr−1; Byrne et al., 2010), which include both anthropogenic and natural variations.

In addition, Ωaragonite and Ω(calcite) in the 26.8–27.0σθ layer significantly decreased at rates of −0.004 to −0.005 yr−1 and −0.006 to −0.008 yr−1, respectively, during our study period (Fig. 5, Table 1). These subsurface rates are slower than rates in subtropical mode water (−0.034 Ωaragonite yr−1) or in subsurface waters of the subarctic region (north of 40° N) along 179° E and 152° W (about −0.007 Ωaragonite yr−1 and −0.010 Ω(calcite) yr−1, Murata and Saito, 2012; Feely et al., 2012). In the western subarctic gyre, the significant increase in TA at a rate of 0.5 ± 0.1 µmol kg−1 yr−1 on the 26.9σθ surface (Table 2) can account for the slower decline in Ω and CO3^2− concentration in subsurface waters. In fact, the observed decrease rate of CO3^2− on the 26.9σθ surface (−0.36 µmol kg−1 yr−1) is slower than the rate calculated by using increasing DIC and constant TA (−0.49 µmol kg−1 yr−1); this calculated rate predicts a faster decline of (−0.007 Ωaragonite yr−1, −0.010 Ω(calcite) yr−1) than the observed declines, which is in good agreement with rates in the subarctic region along 179° E and 152° W (Murata and Saito, 2012; Feely et al., 2012). Because one component of TA and DIC is CO3^2−, increases in TA slow the decrease rates of Ωaragonite and Ω(calcite) in intermediate waters.

### 3.2 Acidification around the CaCO3 saturation horizons

Below the mixed layer in the western subarctic region, the calcite saturation horizon (Ω(calcite) = 1, ~185 m) has significantly shoaled at the rate of 2.9 ± 0.9 m yr−1 (p < 0.001), whereas the aragonite saturation horizon (Ωaragonite = 1) has remained constant at about 120 m depth (Fig. 4). This shoaling rate of Ω(calcite) = 1 is nearly three times higher than that in the Alaskan gyre between 40° N and 50° N from 1991 to 2006 (~1 m yr−1) (Feely et al., 2012). One cause of upward migration of the saturation horizon is the decrease of CO3^2− concentration, because oceanic CO2 uptake lowers Ω due to declining CO3^2−. At the depth where Ω(calcite) = 1, a significant decrease in CO3^2− at a rate of −0.03 ± 0.01 µmol kg−1 yr−1 (p < 0.005) (Fig. 4) has thus caused shoaling of Ω(calcite) = 1.

Between 26.7σθ and 27.0σθ, that is, around the depth where Ωaragonite = 1 (~26.8σθ), pH declined from 1997 to 2011 (Fig. 5, Table 1). The pH decrease rate in the 26.7–27.0σθ layer (~0.003 to ~0.005 yr−1) was faster than the acidification rate expected from equilibration with the atmosphere (−0.002 yr−1). Similarly, the rate of [H+]F increase in the in the 26.7–27.0σθ layer (1.0 × 10−10 to 2.9 × 10−10 mol kg−1 yr−1) was faster than the acidity rate expected from equilibration with the atmosphere (0.4 × 10−10 mol kg−1 yr−1) (Table 1). Acidity ([H+]F) is on a logarithmic scale as pH (−log10[H+]F). Their rates of pH decline at various depths actually represented different rates of [H+]F accumulation. Decadal change of maximum pH decline in the subsurface water (−0.05) corresponds to an approximately 10% increase in [H+]F. The elevated acidification rate at 26.9σθ (Table 1) is higher than the previous observed rate in the open North Pacific (at 250 m depth at Station ALOHA, −0.003 pH(θ) in situ yr−1; Dore et al., 2009, and in the upper 500 m along 152° W between Hawaii and Alaska, −0.004 pH(θ) in situ yr−1; Byrne et al., 2010), which include both anthropogenic and natural variations.

In addition, Ωaragonite and Ω(calcite) in the 26.8–27.0σθ layer significantly decreased at rates of −0.004 to −0.005 yr−1 and −0.006 to −0.008 yr−1, respectively, during our study period (Fig. 5, Table 1). These subsurface rates are slower than rates in subtropical mode water (−0.034 Ωaragonite yr−1) or in subsurface waters of the subarctic region (north of 40° N) along 179° E and 152° W (about −0.007 Ωaragonite yr−1 and −0.010 Ω(calcite) yr−1, Murata and Saito, 2012; Feely et al., 2012). In the western subarctic gyre, the significant increase in TA at a rate of 0.5 ± 0.1 µmol kg−1 yr−1 on the 26.9σθ surface (Table 2) can account for the slower decline in Ω and CO3^2− concentration in subsurface waters. In fact, the observed decrease rate of CO3^2− on the 26.9σθ surface (−0.36 µmol kg−1 yr−1) is slower than the rate calculated by using increasing DIC and constant TA (−0.49 µmol kg−1 yr−1); this calculated rate predicts a faster decline of Ω (~0.007 Ωaragonite yr−1, −0.010 Ω(calcite) yr−1) than the observed declines, which is in good agreement with rates in the subarctic region along 179° E and 152° W (Murata and Saito, 2012; Feely et al., 2012). Because one component of TA and DIC is CO3^2−, increases in TA slow the decrease rates of Ωaragonite and Ω(calcite) in intermediate waters.

### 3.3 Impact of other properties on the pH decrease rate on the 26.9σθ surface

Because we found that the pH decrease rate was enhanced between 26.8σθ and 27.0σθ, we focus on the factors controlling the largest pH decrease rate, on 26.9σθ (~0.0051 pH(θ) in situ yr−1, Table 1), which was at the depth of the temperature maximum (e.g., Wakita et al., 2010a). In this study, we calculated pH(θ) in situ from pressure, temperature, salinity, phosphate, silicate, DIC, and TA; therefore, the pH decrease reflects significant temporal changes in these properties on 26.9σθ from 1997 to 2011 (Table 2). Therefore, to investigate which properties dominantly controlled pH changes, we expressed the pH change (decrease) from 1997 to 2011 (ΔpH)


Table 1. Rates of decrease for pH, free hydrogen ion ([H$^+$]$_F$) and $\Omega$ in the western subarctic gyre from 1997 to 2011.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Depth(ave.) [m]</th>
<th>pH$_{\text{in situ}}$</th>
<th>pH$_F^{25}$</th>
<th>[H$^+$]$_F$ [mol kg$^{-1}$ yr$^{-1}$]</th>
<th>$\Omega_{\text{Aragonite}}$</th>
<th>$\Omega_{\text{Calcite}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.7$\sigma_\theta$</td>
<td>144.0 ± 13.9</td>
<td>-0.0022 ± 0.0010</td>
<td>-0.0019 ± 0.0009</td>
<td>1.0 ± 0.4 × 10$^{-10}$</td>
<td>(p &lt; 0.05)</td>
<td>(p &lt; 0.05)</td>
</tr>
<tr>
<td>26.8$\sigma_\theta$</td>
<td>172.4 ± 19.1</td>
<td>-0.0036 ± 0.0009</td>
<td>-0.0030 ± 0.0008</td>
<td>1.8 ± 0.4 × 10$^{-10}$</td>
<td>(p &lt; 0.0001)</td>
<td>(p &lt; 0.0001)</td>
</tr>
<tr>
<td>26.9$\sigma_\theta$</td>
<td>215.3 ± 27.9</td>
<td>-0.0050 ± 0.0010</td>
<td>-0.0049 ± 0.0009</td>
<td>2.7 ± 0.6 × 10$^{-10}$</td>
<td>(p &lt; 0.0005)</td>
<td>(p &lt; 0.0005)</td>
</tr>
<tr>
<td>27.0$\sigma_\theta$</td>
<td>279.8 ± 33.3</td>
<td>-0.0045 ± 0.0009</td>
<td>-0.0036 ± 0.0008</td>
<td>3.2 ± 0.6 × 10$^{-10}$</td>
<td>(p &lt; 0.0001)</td>
<td>(p &lt; 0.0001)</td>
</tr>
</tbody>
</table>

Table 2. Rates of change in DIC and other parameters on the 26.9$\sigma_\theta$ surface in the western subarctic gyre. Error values are the standard error of the slope of the linear regression.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Rates [units]</th>
<th>p value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>-1.72 ± 0.58 [db yr$^{-1}$]</td>
<td>&lt; 0.005</td>
</tr>
<tr>
<td>Temperature</td>
<td>0.025 ± 0.005 [°C yr$^{-1}$]</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Salinity</td>
<td>0.0027 ± 0.0006 [yr$^{-1}$]</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.011 ± 0.002 [µmol kg$^{-1}$ yr$^{-1}$]</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Silicate</td>
<td>0.23 ± 0.06 [µmol kg$^{-1}$ yr$^{-1}$]</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>TA</td>
<td>0.5 ± 0.1 [µmol kg$^{-1}$ yr$^{-1}$]</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>DIC</td>
<td>2.0 ± 0.3 [µmol kg$^{-1}$ yr$^{-1}$]</td>
<td>&lt; 0.001</td>
</tr>
</tbody>
</table>

as the sum of the change in each property, as follows:

$$\Delta \text{pH} = (\partial \text{pH}/\partial \text{Press}) \Delta \text{Press} + (\partial \text{pH}/\partial S) \Delta S + (\partial \text{pH}/\partial T) \Delta T + (\partial \text{pH}/\partial \text{PO}_4) \Delta \text{PO}_4 + (\partial \text{pH}/\partial \text{Si}) \Delta \text{Si} + (\partial \text{pH}/\partial \text{DIC}) \Delta \text{DIC} + (\partial \text{pH}/\partial \text{TA}) \Delta \text{TA},$$

(5)

where Press, $T$, and $S$ are pressure (unit: db), temperature (unit: °C), and salinity, respectively. $\Delta \text{Press}$, $\Delta T$, $\Delta S$, $\Delta \text{PO}_4$, $\Delta \text{Si}$, $\Delta \text{DIC}$, and $\Delta \text{TA}$ show the changes in Press, $T$, $S$, $\text{PO}_4$, Si, DIC, and TA, respectively. In the actual calculation, we evaluated the rate of pH change by allowing one parameter to vary while using mean values for the other parameters. For example, we estimated the contribution of $\Delta \text{DIC}$ to $\Delta \text{pH}$ ($\partial \text{pH}/\partial \text{DIC}$ $\Delta \text{DIC}$) by calculating $\Delta \text{pH}$ using the increasing values of DIC from 1997 to 2011 and mean values for the other parameters ($-0.0064 ± 0.0010$ pH$_{\text{in situ}}$ yr$^{-1}$, $p < 0.001$) and then computed the impact of $\Delta \text{DIC}$ on $\Delta \text{pH}$ to be 127% by dividing the $\Delta \text{DIC}$ contribution by the rate of pH decline on 26.9$\sigma_\theta$ ($-0.0064/0.0010 = 100$) (Fig. 6).

The results of these calculations show that $\Delta \text{DIC}$ had the largest negative impact on $\Delta \text{pH}$ (127 ± 32%) and $\Delta \text{TA}$ had the largest positive impact (−34 ± 8%) (Fig. 6). The increases in DIC and in temperature ($\Delta T$ impact, 8 ± 2%) over time enhanced the rate of acidification. The contribution of $\Delta T$ (−0.0004 ± 0.0001 pH$_{\text{in situ}}$ yr$^{-1}$) was equivalent to the difference between the in situ and fixed temperature pH trends (Table 1). $\Delta \text{TA}$ and shoaling of the 26.9$\sigma_\theta$ isopycnal surface ($\Delta \text{Press}$, −2 ± 1%) inhibited the pH decrease. The impacts of $\Delta S$, $\Delta \text{PO}_4$, and $\Delta \text{Si}$ were negligibly small (−0.001). In addition, nDIC, which normalized to a salinity of 35, in the 26.9$\sigma_\theta$ surface significantly increased at rate of 1.8 ± 0.3 µmol kg$^{-1}$ yr$^{-1}$ ($p < 0.001$). This value is consistent with DIC increase at the same isopycnal surface (Table 2, Fig. 7). Thus, the lack of a $\Delta S$ contribution means that the influence of local changes evaporation and precipitation was very low; therefore, there is no need to use salinity-normalized values of DIC, TA, and nutrients to correct for such an effect.

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3.4 Contribution of the DIC increase to enhanced acidification

As shown in Sect. 3.3, ΔDIC dominantly accounted for the faster pH decline on 26.9σθ. We investigated factors affecting the DIC increase rate at this depth (2.0 ± 0.3 µmol kg⁻¹ yr⁻¹, p < 0.001) (Fig. 7, Table 2).

Changes of DIC along an isopycnal surface of subsurface water are controlled by the gas exchange of CO₂ at the air–sea interface (DIC_air–sea), the decomposition of organic matter (DIC_org) and the dissolution of calcium carbonate (DIC_CaCO₃). We can express the observed DIC change (ΔDIC_obs), as follows (e.g., Sabine et al., 2002):

\[
\Delta DIC_{\text{obs}} = \Delta DIC_{\text{air–sea}} + \Delta DIC_{\text{org}} + \Delta DIC_{\text{CaCO}_3}
\]

(6)

ΔDICOrg is calculated as following,

\[
\Delta DIC_{\text{org}} = (C_{\text{org}}/ - O_2)\Delta AOU_{\text{obs}},
\]

(7)

where ΔAOUobs is the observed rate of the AOU change. AOU significantly increased at a rate of 1.8 ± 0.4 µmol kg⁻¹ yr⁻¹ (p < 0.0001) (Fig. 7). ΔDICorg was calculated to be 1.2 ± 0.3 µmol kg⁻¹ yr⁻¹.

The dissolution of CaCO₃ neutralizes CO₂ taken up by seawater and increases TA via the reaction (CaCO₃ + CO₂ + H₂O → 2HCO₃⁻ + Ca²⁺). We evaluated ΔDIC_CaCO₃ as ΔCaCO₃ (Feely et al., 2004):

\[
\Delta DIC_{\text{CaCO}_3} = \Delta CaCO_3 = 0.5(TA - TA^*)
\]

(8)

\[ + 0.63(16/170AOU), \]

where TA° is preformed TA, calculated by using the equation of Sabine et al. (2002). ΔDIC_CaCO₃ significantly increased at a rate of 0.3 ± 0.1 µmol kg⁻¹ yr⁻¹ (p < 0.0001) (Fig. 7).

This result, which is consistent with the 50% increase of TA on the same isopycnal surface (Table 2), suggests that the dissolution of CaCO₃ particles increased as a result of the enhanced acidification caused by anthropogenic CO₂ and the AOU increase below the depth of θ = 1 (120–200 m); these saturation depths are shallower than the saturation depth in the open North Pacific (Feely et al., 2004).

By subtracting ΔDICorg and ΔDIC_CaCO₃ from ΔDIC_obs according to Eq. (6), we estimated ΔDIC_air–sea to be 0.5 ± 0.4 µmol kg⁻¹ yr⁻¹. This rate is indistinguishable from that expected under condition of seawater/atmosphere equilibrium (0.7 µmol kg⁻¹ yr⁻¹), when calculated from the increase of atmospheric CO₂ (2.1 ppm yr⁻¹) from 1997 to 2011 at 44.4°N (Conway et al., 2012) and constant TAwin. We assumed that ΔDIC_air–sea indicates the DIC increase due to the uptake of anthropogenic CO₂ (ΔDICanth). ΔDIC_air–sea includes the DIC content of waters in equilibrium with pre-industrial atmospheric CO₂ (280 ppmv) (DIC_eq280) and the DIC content due to the of air–sea disequilibrium CO₂ effect (DIC_diseq). DIC_eq280 remains constant over time and its trend can be cancelled out. We also can neglect temporal change of DIC_diseq on 26.9σθ, i.e., ΔDIC_diseq = 0, because ΔDIC_air–sea on 26.9σθ (0.5 µmol kg⁻¹ yr⁻¹) was lower than the ΔDICwin increase (0.9 µmol kg⁻¹ yr⁻¹) which was affected by the increase of anthropogenic CO₂ and the reduction of CO₂ emission in winter (Wakita et al., 2010a).

The contribution of ΔDIC (2.0 ± 0.3 µmol kg⁻¹ yr⁻¹) is thus accounted for by ΔDICorg (60 ± 17%), ΔDIC_anth (25 ± 22%) and ΔDIC_CaCO₃ (15 ± 5%). Acidification of intermediate water in the western subarctic gyre (−0.0051 ± 0.0010 pH per yr) was enhanced by increases in the decomposition of organic matter (75 ± 29%) and, in the anthropogenic CO₂ uptake (31 ± 29%), by the increased dissolution of CaCO₃ particles (19 ± 8%) and by water temperature warming (8 ± 2%), and it was inhibited by the TA increase (−34 ± 8%) and the shoaling of the isopycnal surface (−2 ± 1%). Because the ΔDIC_CaCO₃ is equivalent to ∼50% increase of TA, the enhanced contribution of the increased dissolution of CaCO₃ particles to faster pH decline could offset the inhibited contribution of TA increase. Non–anthropogenic CO₂ factors correspond to ΔDICorg evaluated from AOU increase and must also contribute to the pH decrease, independently of the uptake of anthropogenic CO₂. The non–anthropogenic CO₂ contribution dominantly accounted for the enhanced acidification of intermediate water rather than anthropogenic CO₂ uptake, but our value might be an overestimate. This is because the long-term trends and bi-decadal oscillations of AOU in subsurface waters in the Northwestern Subarctic Pacific Ocean have been reported (ex., Ono et al., 2001; Osafune and Yasuda, 2006; Watanabe et al., 2008, Takatani et al., 2012). In our data, collected during 1997–2011, AOU varies on a shorter than bi-decadal cycle and the AOU increase on 26.9σθ (1.8 ± 0.4 µmol kg⁻¹ yr⁻¹) was twice that from 1968 to 1998 in the Oyashio region near the western
subarctic gyre (0.8 ± 0.3 µmol kg⁻¹ yr⁻¹) (Ono et al., 2001). Considering this context and the stoichiometric ratio of carbon to oxygen from organic matter decomposition, the minimum possible contribution of non-anthropogenic CO₂ (0.8 × 117/170 = 0.55 µmol kg⁻¹ yr⁻¹) is the same as the anthropogenic CO₂ uptake (0.5 ± 0.4 µmol kg⁻¹ yr⁻¹) in the western subarctic gyre, which is the same the uptake rate in intermediate water along 152° W during 1991–2006 (Byrne et al., 2010) and 179° E during 1993–2007 (Murata and Saito, 2012). Thus, the enhanced acidification (pH decrease) between 200 and 300 m depth in this region reflects both anthropogenic CO₂ and non-anthropogenic CO₂ contribution, which will not affect the spatial distributions of acidification rates (Murata and Saito, 2012).

Temporal changes of AOU in the subsurface waters thus reflect those of both physical processes such as ocean circulation and ventilation, and biological processes such as the remineralization of organic matter. At first, we examine the stoichiometric ratios of phosphorus and nitrogen to oxygen during the decomposition of organic matter ((P/O₂), (N/O₂)) in the 26.9 σθ surface, because phosphate, nitrate, AOU increased significantly over the period of observation (0.011 ± 0.002 µmol kg⁻¹ yr⁻¹, p < 0.0001, and 0.24 ± 0.04 µmol kg⁻¹ yr⁻¹, p < 0.0001, 1.8 ± 0.4 µmol kg⁻¹ yr⁻¹, p < 0.0001 respectively). Based on each increase rate, (P/O₂) and (N/O₂) are calculated to be 171 ± 38 (0.011/1.8) and 23 ± 4 (0.24/1.8), which are nearly consistent with previous values (170 ± 10, 16 ± 1, Anderson and Sarmiento, 1994). This result indicates that remineralization of organic matter have remained constant. Thus, the increase of AOU on 26.9 σθ will be caused by physical processes such as the increase of residence time in the intermediate water.

The changes of physical processes will be dominant in causing the AOU changes (e.g., Deutsch et al., 2005, Mecking et al., 2008). The temporal variations of AOU in the 26.7–27.2 σθ layer in the Oyashio region and a wintertime wind stress curl anomaly in this region are negatively and positively correlated, respectively, with the bi-decadal component of the North Pacific Index (Ono et al., 2001; Ishii and Hanawa, 2005). Because AOU was positively correlated with DIC in the subsurface waters of the western subarctic gyre (r = 0.99) due to the decomposition of organic matter, DIC might also exhibit a bi-decadal oscillation. In addition, in this region, the weakening of the overturning circulation due to reduced winds since the 1970s causes DIC to increase by AOU increase rather than anthropogenic CO₂ uptake (Feely et al., 2012). Considering that minimum estimates of anthropogenic CO₂ and non-anthropogenic CO₂ contributions are of similar magnitude, at least half of the pH decrease rate in the intermediate waters may be related to atmospheric forcing change related to the climate variations.

4 Conclusions

Anthropogenic CO₂ uptake and natural variability due to temporal changes in physical and biogeochemical processes affect acidification in the both the winter mixed layer and intermediate waters in the western subarctic gyre. In the winter mixed layer, pH decreased at –0.0011 ± 0.0004 pH units year⁻¹ from 1997 to 2011, whereas Ωaragonite, Ωcalcite, and CO₂⁻⁻⁻ remained unchanged. This decreasing trend of pH was slower than that predicted based on equilibration of atmospheric CO₂ with the seawater (–0.002 pH units year⁻¹) and slower than decrease rates in other regions (Dore et al., 2009; Midorikawa et al., 2010; Ishii et al., 2011; Byrne et al., 2010). We attribute this lower rate to a reduction of CO₂ emission in winter caused by increased TAwin. Although the correlation of TAwin with the depth of the winter mixed layer (r = 0.37) is quite small, it is significant.

Below the mixed layer, the calcite saturation horizon (Ωcalcite = 1) has shoaled at 2.9 ± 0.9 m yr⁻¹ because of declines in CO₂⁻⁻⁻ (–0.03 ± 0.01 µmol kg⁻¹ yr⁻¹), and the acidification rate at ~200 m depth (–0.0051 ± 0.0010 pH units year⁻¹) was larger than ever reported in the open North Pacific during the study period (e.g., Dore et al., 2009; Byrne et al., 2010). The enhanced pH decline reflected not only the uptake of anthropogenic CO₂ but also natural variability evaluated from the increase in AOU, which suggests that the dissolution of CaCO₃ particles increased. The TA increase due to this increase of CaCO₃ dissolution inhibited the decrease rate of Ωaragonite and Ωcalcite in the intermediate water (–0.004 to –0.005 yr⁻¹ and –0.006 to –0.008 yr⁻¹).

The acidification observed at K2 and KNOT will affect carbonate forming biota in the surface and subsurface waters of the western subarctic region. However, our detection of the pH decrease in the winter mixed layer is not enough to clarify the impact of acidification on biological production and ecosystems in the entire western subarctic gyre. Therefore, the temporal variation of the pH in the mixed layer needs to be evaluated by using more accurate data from a longer time series. Moreover, the CO₂ efflux from the winter mixed layer and the enhanced pH decrease in the subsurface waters must be related to changes in atmospheric forcing as well as the anthropogenic increase in atmospheric CO₂. Additional time-series data are required to investigate the relationships among temporal variability of pH, oceanic physical processes, and atmospheric forcing/climate index.

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