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**A high-resolution mapping of ocean carbon species
in the high latitude North Pacific**

(北太平洋高緯度海域における海洋炭酸物質
の高解像度マッピング)

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HOKKAIDO UNIVERSITY**

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Tables of Contents

Chapter 1	General introduction	1
Chapter 2	Spatiotemporal distribution of sea water carbon species	11
2.1	Introduction	11
2.2	Data and Methods	14
2.3	Parameterizations of carbon species over the North Pacific	16
2.4	Application of the parameterizations of TA, DIC and pH ₂₅ to the time-series data from Argo profiling floats	24
2.5	Concluding remarks	25
	Tables	26
	Figures	30
	References	41
Chapter 3	Quasi-real-time and high-resolution spatiotemporal distribution of ocean anthropogenic CO₂ (C_{ant})	45
3.1	Introduction	45
3.2	Improved parameterizations of TA, DIC and pH	48
3.3	Estimation of C _{ant} using Argo-based DO, T and S data	50
3.4	High-resolution distributions of carbon species and C _{ant}	54
	Tables	56
	Figures	57
	References	64
Chapter 4	Effect of vertical mixing on anthropogenic carbon variation between Okhotsk Sea and North Pacific	67
4.1	Introduction	67
4.2	Data and Methods	70

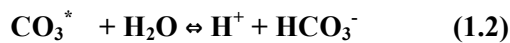
4.3 Results and Discussion	74
4.4 Concluding remarks	77
Tables	78
Figures	79
References	84
Chapter 5 General conclusion	87
Acknowledgement	

Chapter 1

General introduction

Carbon dioxide (CO₂) is the most important greenhouse gas after water vapor in the atmosphere. Its concentration has increased since 1750s because of human activity. In 2011 the concentration of CO₂ was 391 ppm and exceeded the pre-industrial levels by 40% [IPCC, 2013] (Figure.1 (a)). The ocean has played an important role as a sink of anthropogenic CO₂, absorbing almost one-fourth of the CO₂ released by anthropogenic activities since the 1750s [Le Quere et al., 2014]. Direct measurements on ocean time-series stations showed that pH decreased with rates ranging between -0.0014 and -0.0024 yr⁻¹ (Figure 1.1(b)) [Bates et al., 2014; Dore et al., 2009; IPCC, 2013; Santana-Casiano et al., 2007]. The increasing absorption of anthropogenic CO₂ has also critically affected marine organisms through ocean acidification by reducing the ocean's capacity to buffer CO₂ [Doney et al., 2009].

In the ocean, CO₂ exists in three different inorganic forms: free CO₂ aqueous CO₂, HCO₃⁻ and CO₃²⁻. The reactions that occur when CO₂ dissolves in seawater can be represented by the following series of equilibrium equations:



The dissolved inorganic carbon (DIC) in seawater is defined as

$$\text{DIC} = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (1.4)$$

where $[\text{CO}_2^*]$ represents the total concentration of all unionized CO_2 , whether they are present as H_2CO_3 or as CO_2 . The DIC in a seawater sample can be directly measured by acidifying the sample, and extracting the CO_2 gas that is produced and measuring its amount.

The total alkalinity (TA) of a seawater sample is a form of mass-conservation relationship for hydrogen ion. It is defined as “the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10.0-4.5$ at 25°C and zero ionic strength) over proton donors (acids with $K > 10.0-4.5$) in one kilogram of seawater sample” [Dickson *et al.*, 2007].

$$\begin{aligned} \text{TA} = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{H}_3\text{SiO}_4^-] + [\text{NH}_3] \\ & - [\text{HS}^-] \dots - [\text{H}^+]_{\text{free}} - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] + \dots \end{aligned} \quad (1.5)$$

To understand how and where the carbon chemistry of the ocean is changing, oceanographers have collected carbon chemistry data, such as alkalinity (TA), dissolved inorganic carbon (DIC), and pH, with high precision throughout the global ocean from the sea surface to the bottom water on a decadal scale, since the late several decades of the last century, primarily from research vessels [Feely *et al.*, 2009]. Ship-based carbon chemistry data, however, cannot provide detailed temporal information, such as annual, seasonal, and monthly variability, and the spatial resolution is also low. Time-series observations of long-term oceanic CO_2 variations are available from some representative

regions, but time-series observation stations are sparsely distributed in the global ocean. To overcome these problems and complement the observational data, researchers have developed parameterizations and models of oceanic CO₂ that use other hydrographic properties, such as dissolved oxygen (DO), temperature (T), salinity (S), chlorophyll-*a*, and nitrate (NO₃⁻) content, which are available with a higher spatial and temporal resolution than carbon chemistry data, to clarify spatiotemporal changes in the carbon chemistry of the ocean [Juranek *et al.*, 2011; Kim *et al.*, 2015; Lee *et al.*, 2006; Nakano and Watanabe, 2005; Takatani *et al.*, 2014].

Recently, Argo profiling floats with global coverage have been developed that automatically measure hydrographic data (DO, T, S, chlorophyll-*a*, NO₃⁻), with extremely high resolution every 1-2 weeks [Thierry, *et al.*, 2015, 2016]. Globally, more than 3000 Argo profiling floats with T and S sensors are currently deployed, and about 8% are also equipped with DO sensors. By applying ocean carbon chemistry parameterizations to hydrographic data from Argo profiling floats, it is possible to map the spatiotemporal distribution of oceanic carbon chemistry in quasi-real-time easier at high resolution.

In the subarctic North Pacific, about 30 Argo profiling floats equipped with DO, T, and S sensors have been deployed. Therefore, we chose this region to test new parameterizations of ocean carbon chemistry using hydrographic data from Argo profiling floats. Without the age information of seawater, we used a new method to estimate the disequilibrium DIC (C_{diseq}) in seawater, which is not only important factor to clarify oceanic anthropogenic CO₂ (C_{ant}) but also a useful indicator to estimate gas exchange of various gases at the air-sea interface. Using the parameterized TA and DIC values along with oceanic carbon chemistry and thermodynamics, we calculated the quasi-real-time distribution of C_{ant} at high-resolution and examined the change in C_{ant} in this region.

By using our parameterization method with Argo profiling floats or other automatic sensor datasets of DO, T, S, and P, it should be possible in the future to map the distributions of global oceanic CO₂ cycle parameters at high resolution.

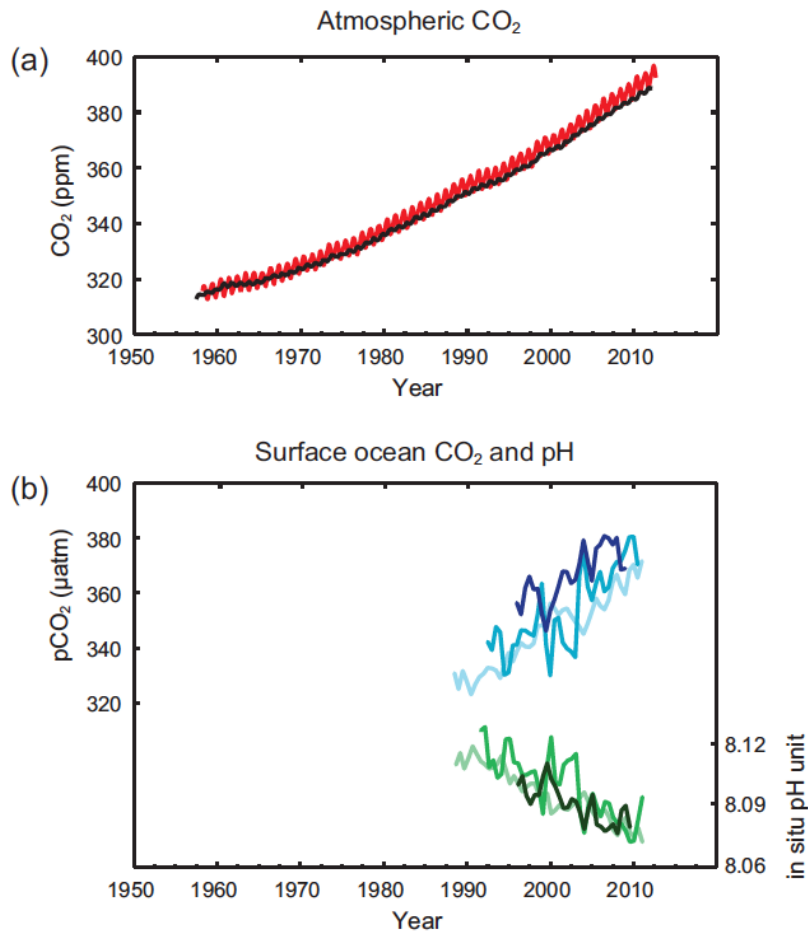


Figure 1.1 Multiple observed indicators of a changing global carbon cycle: (a) atmospheric concentrations of CO₂ from Mauna Loa (19°32'N, 155°34'W – red) and South Pole (89°59'S, 24°48'W – black) since 1958; (b) partial pressure of dissolved CO₂ at the ocean surface (blue curves) and in situ pH (green curves), a measure of the acidity of ocean water. Measurements are from three stations from the Atlantic (29°10'N, 15°30'W – dark blue/dark green; 31°40'N, 64°10'W – blue/green) and the Pacific Oceans (22°45'N, 158°00'W – light blue/light green). [IPCC, 2013]

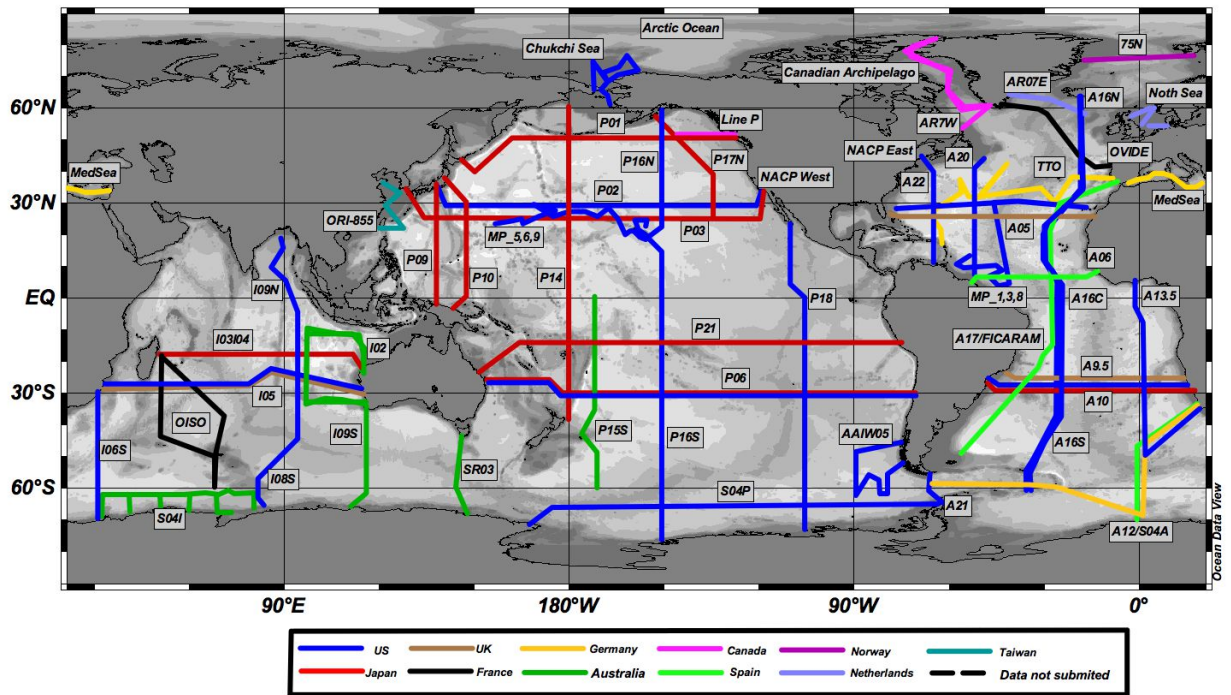


Figure 1.2 Observational repeat lines of WOCE/CLIVAR from 1990s. [CDIAC, <http://cdiac.ornl.gov>]

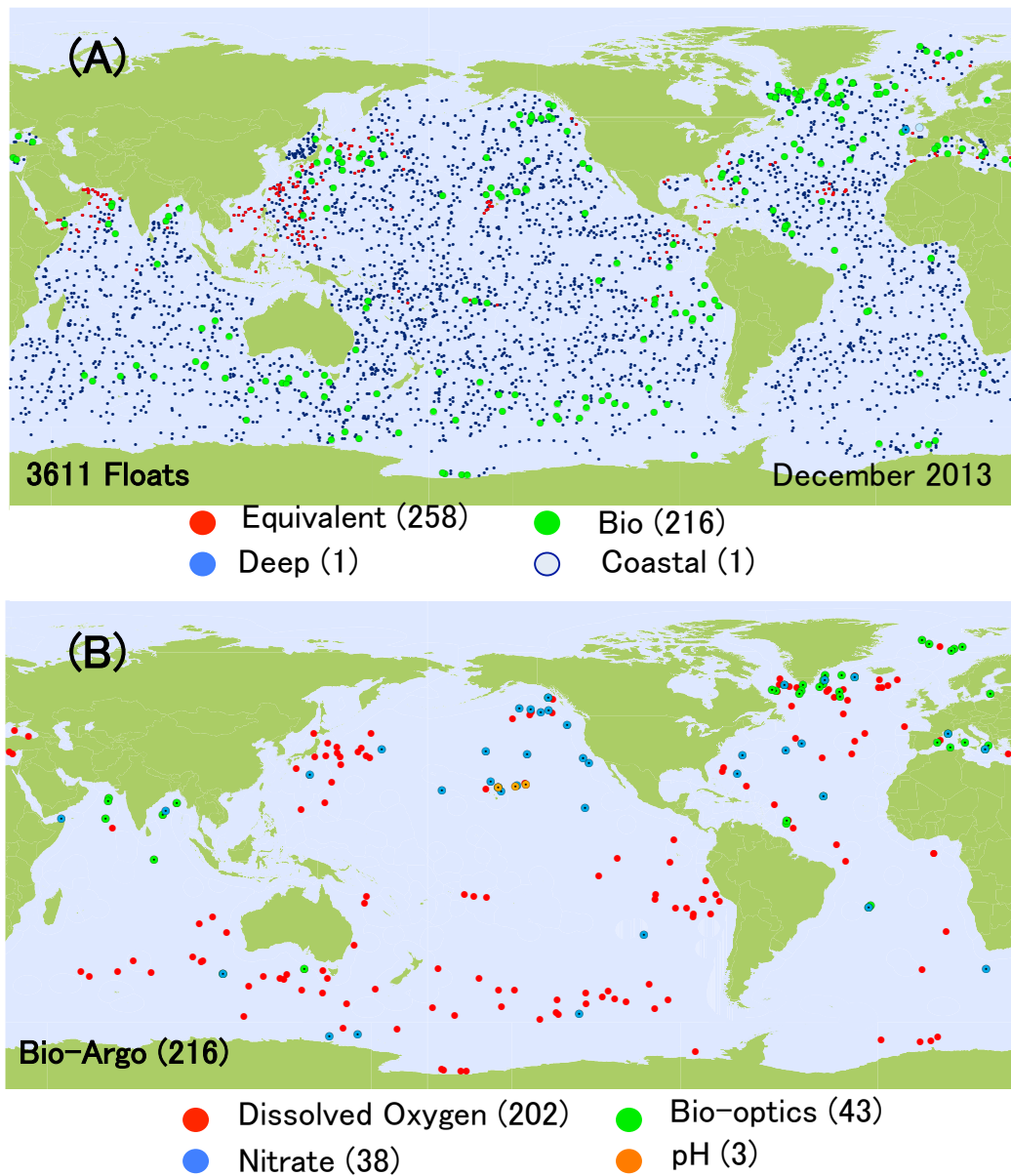


Figure 1.3 Distribution of Argo floats in the global ocean. [*Argo Information Center, 2013*]

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Chapter 2

Spatiotemporal distributions of sea water carbon species

2.1 Introduction

Marine carbon systems are known to control both ocean biogeochemistry cycles and climate. Given rising level of anthropogenic carbon, the ocean carbon cycle may be experiencing significant change [Alin *et al.*, 2012]. As an important buffer action for the environmental change, the ocean has absorbed almost one fourth of the CO₂ released by anthropogenic activities since the industrial revolution [Le Quere *et al.*, 2014]. The oceanic uptake of CO₂ changes its chemical equilibrium, which consequently decreases the seawater pH. *Intergovernmental Panel on Climate Change* 2013 (IPCC, 2013) reported that oceanic uptake of anthropogenic carbon since 1750 has led to the ocean becoming more acidic, with an average decrease in surface pH of 0.1 units. Decreasing surface ocean pH, in combination with rising surface temperatures has a strong effect on the marine organisms and acts to reduce the ocean buffer capacity for CO₂ [Doney *et al.*, 2009]. Therefore, it is important to understand how and where does the pH change in the ocean.

Time-series observations from Station Aloha in the North Pacific subtropical region have shown a decrease in pH of 0.002 units per year over the last several decades [IPCC, 2013]. However, the similar time-series mooring observations of pH in the global ocean are scarce. In order to have the detailed information of ocean acidification, it is necessary to obtain the spatiotemporal distribution of seawater pH in high precision on a global scale. The marine CO₂ system consists of total alkalinity (TA), dissolved inorganic carbon (DIC), pH, and fugacity of CO₂ ($f\text{CO}_2$) [Dickson *et al.*, 2007]. Measuring two of these properties, we can calculate the others. Since the 1990s, most ocean researchers measured TA and DIC with high precisions from the sea surface to the bottom water over the global ocean. Their data were available on an approximately decade scale from the international programs such as World Ocean Circulation Experiment (WOCE) and CLimate VARIability and

predictability (CLIVAR). Unfortunately, the observational data cannot provide more detailed temporal changes (e.g., such as annual, seasonal and monthly variability).

Developing a parameterization technique and applying it to other hydrographic properties (e.g., Dissolved Oxygen (DO), Temperature (T), Salinity (S), chlorophyll-a and nitrate (NO_3^-)), the carbonate species in the ocean can be reconstructed by empirical equations within a higher spatial and temporal resolution in carbon chemistry than the traditional ship-based method [Feely *et al.*, 2009; Juranek *et al.*, 2011; Nakano and Watanabe, 2005; Touratier and Goyet, 2011]. However, previous empirical equations were limited only to the surface [Nakano and Watanabe, 2005] or to a narrow region such as the North East Pacific subpolar region [Juranek *et al.*, 2011]. Kim *et al.*, (2015) also discussed the regionally varying multiple linear regression parameterization (rMLR) for the saturation state of aragonite (Ω_{AR}) at a grid size of $5^\circ \times 5^\circ$ for the North Pacific region. However, it is difficult to determine the Ω_{AR} value of the boundary of each grid, because there are several different of c_{AR} at the same position. Developing a single multiple linear regression parameterization (sMLR) of carbonate species would overcome this problem and allow us to understand the detailed spatiotemporal behavior of ocean carbon system.

In the North Pacific subpolar region, with the weakening of the vertical water mixing [e.g., Watanabe *et al.*, 2001], recent biological activity has been decreased [e.g., Sugimoto and Tadokoro., 1997; Schell., 2000]. Furthermore, with absorption of CO_2 , organisms that form CaCO_3 shells will decrease in the future [Doney *et al.*, 2009]. In this study, we chose this region to test the application of parameterization technique to clarify ocean carbon chemistry from the surface to the ocean interior on an ocean basin scale.

Changes in the carbonate species of seawater are mainly controlled by the physical and biological processes. Assuming that DO represents one index of the biological processes and T and S represent indices of physical processes, we attempt to use DO, T, and S to reconstruct the concentrations of TA, DIC and pH in the North Pacific subpolar region.

Recently, a new generation of ‘automatic measurement robots’ – Argo profiling floats equipped with DO, T, and S sensors has been developed to measure these hydrographic data automatically every two weeks (Argo website, <http://argo.argo.net/>). More than 3,000 Argo profiling floats are in operation in the global ocean and 200 of these Argo profiling floats were equipped with DO sensors (<http://argo.jcommops.org/maps.html>). In this study, applying our parameterizations to the independent hydrographic dataset obtained from Argo profiling floats in this region, we also tried to obtain the detailed spatiotemporal distribution of pH in almost real-time at a mid-depth over the North Pacific subpolar region.

2.2 Data and Methods

We used all of the available observational carbon chemistry data (TA and DIC) and hydrographic data (DO, T, and S) from CLIVAR and the PACIFIC ocean Interior Carbon (PACIFICA) datasets during the period from 2000 to 2010 (Fig. 2.1; *Suzuki et al.*, 2013). We chose the data from the depth from 40–400 m over the North Pacific subpolar region (40°N–56°N, 145°E–130°W). The data quality of TA and DIC after 2000 were controlled by using Certified Referenced Materials (e.g., which distributed by A. G. Dickson of the Scripps Institution of Oceanography (SIOCRM)) [*Dickson et al.*, 2007]. Therefore, we chose the data after 2000, which would be better precision than those analyzed previously.

Based on the previous studies, we can estimate TA, DIC and pH only in the sea surface by using the parameterizations based on T, S and chlorophyll-a ...[e.g., *Miilero et al.*, 1998; *Lee et al.*, 2000; *Nakano and Watanabe*, 2005, *Lee et al.*, 2006 and *Takakani et al.*, 2014]. However, it was difficult to apply these parameterizations to the vertical distributions of TA, DIC, and pH because there were chlorophyll-a only within seasurface [e.g., *Nakano and Watanabe*, 2005]. Therefore, we here used DO as biological parameter to reconstruct TA, DIC and pH in the ocean interior [*Juranek et al.*, 2011]. In the North Pacific subpolar region, there is large amount of phytoplankton in the surface euphotic zone, especially in the spring [e.g., *Imai et al.*, 2002]. Phytoplankton produces large amount of O₂ and then the O₂ produced by them is exported to the atmosphere. It would also decouple for stoichiometric ratio of O₂ to CO₂ in the sea and this is the reason why we also chose the data under 40 m. Additionally, in the surface mixed layer, the different air–sea gas exchange timescales of O₂ and CO₂ also may decouple for stoichiometric ratio of O₂ to CO₂ in the sea (for a more detail explanation, see section 6.6.5 of *Williams and Follows* (2011)). Therefore, we also excluded the data within the surface mixed layer. We defined the depth of seasonal surface mixed layer as a water depth having the difference of 0.125 σ_θ from the surface density [*de Boyer Montégut et al.*, 2004].

For the independent data to test the parameterizations, we chose the datasets from time-series

monitoring Stations KNOT (44°N, 155°E) and Papa (50°N, 145°W) during the period from 2000 to 2008 (a filled triangle and a filled diamond in Fig. 2.1). In addition, we used the data observed from the No. 255 cruise of Oshoro–maru during the summer of 2013 (OS2013). Here, we used two data points of OS2013 that were OS2013_1 (55 °N, 169 °W) and OS2013_2 (54 °N, 169 °W) (open and filled circles in Fig. 2.1). In this cruise, we collected the OS2013 samples of TA and DIC by a Niskin bottle multiple sampling system with a CTD. We analyzed the TA and DIC samples using the simultaneous measurement in semi-closed–cell method (Kimoto Electric Co., Ltd., ATT-05). The precisions of this method were 0.06% for TA ($\pm 1.3 \mu\text{mol/kg}$) and 0.08% ($\pm 1.6 \mu\text{mol/kg}$) for DIC. Additionally, the value of pH at 25 °C (henceforth referred as pH25) can be calculated by the above TA and DIC, of which precision was of 0.14% ($\pm 0.011 \text{ pH}$) on the seawater scale.

We calculated all of the pH values on the seawater scale, with the measured TA, DIC, T, S, pressure and the constants of *Mehrbach et al.* [1973] refitted by *Dickson and Millero* [1987].

To reconstruct the monthly and seasonally distributions of TA, DIC, and pH25, we used the climatological data of DO, T, and S from World Ocean Atlas 2009 (WOA2009, these data are available from the NODC website, <http://www.nodc.noaa.gov>).

In the North Pacific subpolar region, eleven Argo profiling floats with DO sensors were in operation until January 2014 and each measured DO, S, and T from the sea surface to 1000 m depth; however, several sensors measured DO only in the upper 120 m or 250 depth. Every Argo float had a unique World Meteorological Organization (WMO) code to distinguish themselves [*Carval et al.*, 2014]. The WMO codes of these Argo profiling floats were 4901136, 5903274, 5903405, 5903714, 5903743, 5904028, 5904095, 5904106, 5904108, 5904125 and 5904126 (these data are available from the Argo website, <http://argo.jcommops.org/maps.html> or http://www.jamstec.go.jp/JARGO/index_j.html).

2.3 Parameterizations of carbon species over the North Pacific

2.3.1 Parameterizations of TA, DIC, and pH25 over the North Pacific subpolar region

In general, the F -test is used to validate the usefulness of different parameters in multiple linear regressions. In this study, parameters with F values of more than 2.4 have a significant meaning [Wilks., 2011], indicating that it is useful to obtain an empirical equation in the multiple linear regressions. We obtained the parameterizations for seawater TA, DIC, and pH25 as the following Eqs. (2.1)–(2.3). Henceforth, we referred the predicted values of TA, DIC, and pH25 as TA_{pre} , DIC_{pre} , and $pH25_{pre}$.

$$TA_{pre} = 641.60 - 0.12 DO - 4.38 T + 49.60 S \quad (2.1)$$

$$(n=1201, R^2 = 0.95, RMSE = 7.36 \mu\text{mol kg}^{-1})$$

$$DIC_{pre} = 1113.23 - 0.67 DO - 16.71 T + 38.28 S \quad (2.2)$$

$$(n=1224, R^2 = 0.99, RMSE = 7.12 \mu\text{mol kg}^{-1})$$

$$pH25_{pre} = 6.354 + 0.00162 DO + 0.0335 T + 0.0219 S \quad (2.3)$$

$$(n=1201, R^2 = 0.99, RMSE = 0.018)$$

R^2 and RMSE represent the coefficient of determination and the root mean square error, respectively. We showed the details of these parameterizations in Table 2.1 and Fig. 2.2. In Eqs. (2.1)–(2.3), DO, T, and S had F with more than 2.4 (Table 2.1), indicating that we can use the DO, T and S values to reconstruct TA, DIC, and pH25. We obtained that the R^2 of Eqs. (2.1)–(2.3) were larger than 0.95 (Table 2.1 and Fig. 2.2). We obtained that the RMSEs for the parameterizations of TA, DIC and pH25 were $7.36 \mu\text{mol kg}^{-1}$, $7.12 \mu\text{mol kg}^{-1}$, and 0.018 pH, respectively (Table 2.1 and Fig. 2.2). At Station

KNOT, recent studies have reported that DIC has increased by $1\text{--}2\ \mu\text{mol kg}^{-1}\ \text{year}^{-1}$ due to rising atmospheric CO_2 and change of water ventilation [e.g., *Wakita et al.*, 2005 and *Wakita et al.*, 2010]. *IPCC* (2013) reported that pH has decreased by 0.002 units per year over the last several decades in the North Pacific. Hence, we can reconstruct DIC and pH25 on a decadal scale using our equations. In Fig. 2.2, TA_{pre} deviated from TA_{mea} over $2300\ \mu\text{mol/kg}$ at about 300 m depth. The depth of 300 m was deeper than CaCO_3 saturation depth in the most of North Pacific subpolar region [*Feely et al.*, 2004]. Therefore, it may be caused by CaCO_3 dissolution.

The F value is defined as the ratio of the regression mean squares (MSR) to the mean square errors (MSE) [e.g., *Wilks.*, 2011]. F value is large when MSR is large or MSE is small. That is to say that F value means the strength of the regression. It also means that a strong relationship between the independent variable (e.g., DO, T and S in Eqs. (2.1)–(2.3)) and the dependent variable (e. g., TA_{pre} , DIC_{pre} , and pH25_{pre} in Eqs. (2.1)–(2.3)) will produce a large F value. Hence, in Eq. (2.1), TA showed a stronger correlation with S ($F = 4396$) than T and DO, suggesting that the physical process would affect this process (Table 2.1). In Eqs. (2.2) and (2.3), both DIC and pH25 showed a considerably stronger correlations with DO compared to T and S ($F > 30000$), suggesting that biological process due to remineralization would affect these parameters (Table 2.1).

Applying the values of two fixed values of ocean carbon species with pressure and T to the equilibrium equations of carbon chemistry in the ocean [*Dickson et al.*, 2007], we calculated how TA, DIC, and pH25 changed with the increasing S (Table 2.2). Using the similar method, we also calculated how TA, DIC and pH25 changed with the increasing T (Table 2.2). Based on the effect derived from changing DO, we also considered how remineralization and photosynthesis impacted on TA, DIC, and pH (Table 2.2).

According to the equilibrium equations of carbon chemistry and the remineralization/photosynthesis processes, TA changes reversely with the increase of DO and positively with increases of T and S, respectively (the first and second columns of TA in Table 2.2).

We found that TA changed reversely with the increases of T in our parameterization (the third column of TA in Table 2.2). Since TA had the strongest relationship with S ($F = 4396$, Table 2.1) and there is general positive relationship between the increases of TA and S (Table 2.2), we concluded that our parameterization for TA, Eq. (2.1) is useful for reconstructing the spatial distribution of TA in this region. On the other hand, DIC generally changes negatively with increases of DO, T, and S, respectively (the first and second columns of DIC in Table 2.2). We can also find that DIC has a reverse change with increases of S (the third column of DIC in Table 2.2). Since DIC had the strongest relationship with DO ($F = 39289$) (Table 2.1) and considerably strong relationship with T ($F = 31938$) (Table 2.1), and there is general negative relationship between the increases of DIC and DO and T (Table 2.2), we concluded that our parameterization for DIC, Eq. (2.2) is useful for reconstructing the distribution of DIC in this region. For pH, generally, it has a positive change with increases of DO and negative change with increases of T and S (first and second columns of pH in Table 2.2). We found that pH have a reverse change with increases of T and S (the third column of pH in Table 2.2). Since pH had the strongest relationship with DO ($F = 32791$, Table 2.1) and there is general positive relationship between the increases of pH and DO (Table 2.2), we concluded that our parameterization for pH, Eq. (2.3) is useful for reconstructing the distribution of pH in this region. The results from Table 2.2 coincided with the F -test results (Table 2.1). We can indicate that our equations could be useful for reconstructing TA, DIC and pH25 over the North Pacific subpolar region.

2.3.2 Differences in TA, DIC and pH25 between the observations and parameterizations

In addition, we must evaluate the temporal changes in these parameterizations. Thus, we compared the predicted values and the measured values (or calculated values) of TA, DIC, and pH25 (henceforth, we referred the measured TA and DIC as TA_{mea} and DIC_{mes} , and the calculated pH25 as $pH25_{\text{cal}}$) derived from three independent datasets in observational time-series Stations KNOT and Papa in the western and eastern areas of the North Pacific subpolar region and the hydrographic

samples collected in OS2013 in the north of this region. We showed these results for Station KNOT and Papa in Fig. 2.3, and for OS2013_1 and OS2013_2 in Fig. 2.4. We obtained that the differences between measured values and predicted values for TA, DIC, and pH25 were almost within $10 \mu\text{mol kg}^{-1}$, $10 \mu\text{mol kg}^{-1}$, and 0.05 pH, respectively. Especially, the differences shown in Fig. 2.4 were less than half of those obtained in Fig. 2.3, probably due to the higher precision measurements of TA and DIC by using the modified semi-closed-cell method in this study. The higher precision measurements of TA and DIC will allow us to construct higher precision parameterizations of TA, DIC and pH in the future.

Furthermore, we described the differences separately at Station KNOT, Papa, OS2013_1 and OS2013_2. We estimated the average differences between the predicted and measured values of TA, DIC and pH25 at every observation points at the depth of our parameterizations (Table 2.3). At Station KNOT, the average differences between the predicted and measured values were $1.39 \pm 5.81 \mu\text{mol kg}^{-1}$ for ΔTA ($\text{TA}_{\text{pre}} - \text{TA}_{\text{mea}}$, $n = 242$), $-0.78 \pm 7.48 \mu\text{mol kg}^{-1}$ for ΔDIC ($\text{DIC}_{\text{pre}} - \text{DIC}_{\text{mea}}$, $n = 242$) and 0.017 ± 0.020 pH for ΔpH25 ($\text{pH25}_{\text{pre}} - \text{pH25}_{\text{cal}}$, $n = 242$). At Station Papa, the average differences between the predicted and measured values were $4.92 \pm 8.46 \mu\text{mol kg}^{-1}$ for ΔTA ($n = 72$), $4.79 \pm 3.47 \mu\text{mol kg}^{-1}$ for ΔDIC ($n = 72$) and 0.000 ± 0.039 pH for ΔpH25 ($n = 72$). For OS2013 samples at Station OS2013_1 and OS2013_2, the average differences between the predicted and measured values were $-1.45 \pm 3.60 \mu\text{mol kg}^{-1}$ for ΔTA ($n = 6$), $-4.28 \pm 3.64 \mu\text{mol kg}^{-1}$ for ΔDIC ($n = 6$) and 0.014 ± 0.013 pH for ΔpH25 ($n = 6$). Considering our RMSEs in our parameterizations (Eqs. (2.1)–(2.3)), we could not find any significant differences of ΔTA , ΔDIC and ΔpH25 at these three stations.

According to previous studies [e.g. *Juranek et al.*, 2011 and *Kim et al.*, 2015], the precision of parameterizations would be affected by the input of the fossil fuel CO_2 . We found that the positive residuals of pH25 in the depth of 40-100 m were consistent with these previous results (Fig. 2.3 and Table 2.3).

2.3.3 Comparison between our parameterization and previous study

In order to validate our parameterizations, we also compared our parameterizations with previous study. Over the North Pacific, *Kim et al.*, (2015) proposed a newest and high precision regionally varying multiple linear regression parameterization (hereafter rMLR) of saturation state of aragonite (Ω_{AR}) in the upper water column (50 m – 800 m depth) by using parameters of potential temperature (θ) and apparent oxygen utilization (AOU) at a grid size of $5^\circ \times 5^\circ$. In order to compare Ω_{AR} estimated by rMLR with that estimated by our single MLR parameterizations (hereafter sMLR), we calculated the Ω_{AR} value by using the equilibrium equations of carbon chemistry in the ocean with TA_{pre} and DIC_{pre} estimated by our sMLR and T, S, pressure and the constants of *Mehrbach et al.* [1973] refitted by *Dickson and Millero* [1987]. Here, we compared the difference between predicted Ω_{AR} ($\Omega_{AR, pre}$) and calculated Ω_{AR} (calculated by TA_{mea} and DIC_{mea} , $\Omega_{AR, cal}$) ($\Omega_{AR, cal} - \Omega_{AR, pre}$, $\Delta\Omega_{AR}$) at Stations KNOT, K2, and Papa by using sMLR and rMLR, respectively. We used the same data of DO, T, S, θ for each station. We showed the time-series results in Fig. 2.5 and the average value of $\Delta\Omega_{AR}$ in Table 2.4. We did not find significant differences of $\Delta\Omega_{AR}$ between our sMLR and rMLR at Stations KNOT and K2 (Fig. 2.5(a) – (b) and Table 2.4). We found that $\Delta\Omega_{AR}$ from rMLR was negative and much lower than that from sMLR at Station Papa. That is to say that, in the whole North Pacific subpolar region, sMLR can have a better precision, when we predict Ω_{AR} .

Additionally, when we use the rMLR to predict the Ω_{AR} , we must consider the boundary conditions of each grids. We chose one position in the boundary of four grids of rMLR and apply the seasonal AOU and θ of four grids of the North Pacific subpolar region. Calculating magnitude of the maximum of difference among these four Ω_{AR} values ($\Delta\Omega_{AR, max}$), we can test the effect of the boundary problem on Ω_{AR} . We did this in the western and eastern parts of North Pacific subpolar region, respectively. We found that the maximum of $\Delta\Omega_{AR, max}$ was 0.650 in the eastern part and 0.225 in the western part. We obtained different values of Ω_{AR} in the same position both in the western and eastern. sMLR had just one equation over all the North Pacific subpolar region and it had continuity between each

grids of $5^\circ \times 5^\circ$. Thus, our sMLR did not need to consider the boundary problem of each grid.

Therefore, with the similar $\Delta\Omega_{AR}$, we can draw the Ω_{AR} map more conveniently by using the sMLR, especially for the application to the DO, T, and S data from the Argo profiling float that moved in multiple grids. rMLR can predict Ω_{AR} more spatial than our sMLR. However, sMLR can predict the Ω_{AR} usefully with a higher precision in the whole North Pacific subpolar region and there is no boundary problem.

In the next section, we would describe more detailer distributions of TA_{pre} , DIC_{pre} and $pH25_{pre}$.

2.3.4 Reconstructions of horizontal distributions of TA, DIC and pH25 seasonally over the North Pacific subpolar region using WOA2009

To describe the seasonally variations of TA, DIC and pH25 over the North Pacific subpolar region using our parameterizations, we used the datasets of DO, T and S four seasons datasets (Jan–Mar, Apr–Jun, Jul–Sep and Oct–Dec) of WOA2009 and substituting them to Eqs. (1)–(3).

We showed the distributions of TA_{pre} , DIC_{pre} , and $pH25_{pre}$ at 50 m for four seasons (Fig. 2.6). The spatiotemporal surface distributions of TA_{pre} , DIC_{pre} , and $pH25_{pre}$ had ranges of 2180–2250 $\mu\text{mol kg}^{-1}$ for TA_{pre} , 2000–2150 $\mu\text{mol kg}^{-1}$ for DIC_{pre} , and 7.60–7.95 pH units for $pH25_{pre}$, respectively. TA_{pre} values decreased eastward and it showed steep eastward gradients from October to December, which agreed with the pattern of distribution from the TA climatological data [e.g., *Key et al.*, 2011]. It was also consistent with the change of climatological S in this region [e.g., *Conkright et al.*, 2002]. DIC_{pre} decreased east-southward and had the lowest value during the period from October to December. Conversely, $pH25_{pre}$ changed as an opposite pattern of the DIC, increasing eastward-southward in the subpolar North Pacific region [*Wong et al.*, 2002]. There was highest value for $pH25_{pre}$ during October to December. The pattern of the change in $pH25_{pre}$ in the four seasons was similar with the results of pH predicted at the surface ocean from *Nakano and Watanabe* (2005). The pattern of the change in $pH25_{pre}$ reconstructed in this study may depend on the change of T in the

upper ocean, which increased eastward-southward in the north of 40 °N in the ocean surface.

2.3.5 Reconstructions of changes in vertical distributions of TA, DIC and pH25 monthly at Station KNOT, Papa and OS2013_1 using WOA2009

Moreover, we described monthly changes in vertical distributions of TA_{pre} , DIC_{pre} , and $pH25_{pre}$, which allow us to obtain the information of shorter time scale of changes of these three carbon species in details. Here we obtained the vertical distributions of TA_{pre} , DIC_{pre} and $pH25_{pre}$ on monthly time-scale. We applied the monthly datasets of DO, T, and S from WOA 2009 to our parameterizations (Eqs. (2.1)–(2.3)) over the depth of 50–400 m at three independent stations (Station KNOT, Papa, and OS2013_1) that we mentioned in section 3.2. We also showed the distributions of DO, T, and S at these stations (Figs. 2.7–2.9(a)–(c)).

Station KNOT had a vertical range of 2220–2350 $\mu\text{mol kg}^{-1}$ for TA_{pre} , 2015–2350 $\mu\text{mol kg}^{-1}$ for DIC_{pre} and 7.30–7.75 pH units for $pH25_{pre}$, respectively. All of TA_{pre} , DIC_{pre} and $pH25_{pre}$ varied almost with T the over the upper 100 m. TA_{pre} at the upper 100 m varied from 2220–2250 $\mu\text{mol kg}^{-1}$ and had the highest value during March and the lowest value during October–January. DIC_{pre} at upper 100 m varied from 2015–2150 $\mu\text{mol kg}^{-1}$ and had the highest value around March and the lowest around October. $pH25_{pre}$ at upper 100 m varied from 7.65–7.75 pH units and had the lowest value around March and the highest value during October. The patterns of variations for TA_{pre} and DIC_{pre} in the upper 100 m were consist with the results in the surface mixed layer of previous studies [Wakita *et al.*, 2013]. On the other hand in the deeper layer of below 100 m depth, TA_{pre} , DIC_{pre} , and $pH25_{pre}$ did not dramatically varied compared with the shallower layers but had stronger relationships with DO.

At Station Papa, the vertical distributions of TA_{pre} , DIC_{pre} , and $pH25_{pre}$ had wider ranges than at the other two regions (2190–2325 $\mu\text{mol kg}^{-1}$ for TA_{pre} , 2025–2350 $\mu\text{mol kg}^{-1}$ for DIC_{pre} and 7.35–7.80 pH units for $pH25_{pre}$, respectively). The pattern of the changes in vertical distributions of TA_{pre} , DIC_{pre} and $pH25_{pre}$ at this station were similar with Station KNOT, although TA_{pre} , DIC_{pre} and $pH25_{pre}$ at

Station Papa changed more smoothly than at Station KNOT due to the weaker monthly variations of DO T and S properties. These results were almost consisting with the previous studies [e. g. *Wong et al.*, 2002 and *Wong et al.*, 2010].

At Station OS2013_1, the vertical distributions of TA_{pre} , DIC_{pre} , and $pH25_{pre}$ had narrower ranges (2210–2280 $\mu\text{mol kg}^{-1}$ for TA_{pre} , 2100–2270 $\mu\text{mol kg}^{-1}$ for DIC_{pre} and 7.60–7.40 pH units for $pH25_{pre}$, respectively). This agreed with the smaller change of temperature near the polar region. Unlike Station KNOT and Station Papa, the pattern of the changes in the entire vertical distributions of TA_{pre} , DIC_{pre} , and $pH25_{pre}$ at OS2013_1 were almost similar with the DO distribution though out a year. For example, the intense changes of DO from September to December affected vertical distributions of TA_{pre} , DIC_{pre} , and $pH25_{pre}$.

2.4 Application of the parameterizations of TA, DIC and pH25 to the time-series data from Argo profiling floats

To describe the spatiotemporal distributions of seawater TA, DIC and pH in the North Pacific subpolar region on a shorter time scale such as two-week scale, we applied our parameterizations of TA_{pre} , DIC_{pre} and $pH25_{pre}$ (Eqs. (2.1)–(2.3)) to the time-series of the vertical distributions of DO, T and S measured by the automatic ocean hydrographic sensors in every two weeks from “automatic measurement robots” – Argo profiling floats.

We found that eleven Argo profiling floats that equipped with DO sensor were operated in the western side and Eastern side of North Pacific subpolar regions. We showed two of them (WMO code: 5904028 and 5904106) in this study (Fig. 2.10), because these two floats had DO data deeper than 400 m. The other floats almost had DO data just from surface to shallower 120 m or 250 m and we did not show the results here. The distributions of TA_{pre} , DIC_{pre} , and $pH25_{pre}$ predicted from the Argo data (Fig. 2.10) had larger variations compared with those predicted from climatological DO, T, and S data (Fig. 2.7 and 2.8). However, the spatiotemporal patterns of TA, DIC, and pH25 were almost similar with the results predicted from the climatological data (Fig. 2.9). We also calculated the in situ pH ($pH_{in\ situ, pre}$) and $\Omega_{AR, pre}$ (Fig. 2.10(g)-(h)). According to *Nakano and Watanabe., 2005*, due to the large difference of in situ T and 25°C, the distribution of $pH25_{pre}$ would be similar with T in the surface. Similar with *Nakano and Watanabe., 2005*, $pH25_{pre}$ also changed similar with T vertically than $pH_{in\ situ, pre}$ (Fig. 2.10).

As some previous studies, DO measurements by the Argo sensor are commonly inaccurate by as much as 20 $\mu\text{mol/kg}$ [e.g. *Juranek et al., 2011*]. Here, we did not calibrate the Argo DO data. Even though, we may capture the relative changes of TA, DIC and pH25 biweekly as the existence of the accuracy of Argo DO data. Using our parameterizations with Argo profiling float could be comparable to increasing more time-series monitoring stations in the North Pacific subpolar region.

2.5 Concluding remarks

We found parameterizations to speculate the seawater pH, TA, and DIC in the subpolar North Pacific by using observations of DO, T, and S data that were mainly from previous high quality dataset of hydrographic properties over the ocean interior (400 m). The parameterizations in this study represent the first to reconstruct spatiotemporal vertical distributions of carbon species throughout the ocean interior over the North Pacific subpolar region [Millero *et al.*, 1998; Lee *et al.*, 2000; Lee *et al.*, 2006, Nakano and Watanabe., 2005 and Takatani *et al.*, 2014]. Moreover, the precision of pH in 0.018 pH units in our parameterizations could allow us to predict pH on a decade scale in this region according to the decrease in pH of 0.002 units per year. On the other hand, our parameterizations cannot distinguish the natural and anthropogenic components, because we cannot predict only anthropogenic ocean acidification directly by using our parameterizations.

Furthermore, using Argo or other automatic sensor datasets of DO, T and S, our parameterizations would allow us to estimate the further detailed spatiotemporal vertical distributions of carbon species over the North Pacific subpolar region. However, there were no dataset of calibrated DO, T, and S derived from Argo float dataset for on longer timescale over decadal scale. There were also no enough DO data of Argo floats in the center of this region. However, with future developments in measurement and sensor techniques in the coming years, we could construct parameterizations with higher precision and predict the pH over the whole the North Pacific subpolar region.

Tables

Table 2.1 Summaries of our parameterizations for the TA, DIC, and pH in the North Pacific subpolar region.

	TA (n ^{#c} = 1201)			DIC (n = 1224)			pH25 (n = 1201)		
	R ² ^{#d}	RMSE ^{#e}	F ^{#f}	R ²	RMSE	F	R ²	RMSE	F
DO ^{#a}			1151			39289			32791
T ^{#b}	0.95	7.36	2055	0.99	7.12	31938	0.99	0.018	14742
S ^{#a}			4396			2816			119

#a: Value derived from the discrete Niskin bottles

#b: Value derived from the CTD sensor

#c: Numbers of data

#d: Coefficient of determination

#e: Root mean square error

#f: Value from *F*-test

Table 2.2 Changes in TA, DIC, and pH in the case that one of either DO, T or S increases.

	TA			DIC			pH		
	Carbon Chemistry ^{#b}	remineralization/ photosynthesis ^{#c}	this study ^{#d}	Carbon Chemistry	remineralization/ photosynthesis	this study	Carbon Chemistry	remineralization/ photosynthesis	this study
DO (+) ^{#a}	/	-	-	/	-	-	/	+	+
T (+)	+	/	-	-	/	-	-	/	+
S (+)	+	/	+	-	/	+	-	/	+

#a: Sign “+” means increasing and “-” means decreasing.

#b: Results calculated by the equilibrium equations of carbon chemistry in the ocean on seawater scale [Robbins *et al.*, 2010] with input of the constants of *Mehrbach et al.* [1973] refitted by *Dickson and Millero* [1987].

#c: Results from the remineralization or photosynthesis progress.

#d: Results from our parameterizations (Eqs. (1) – (3))

Table 2.3 The average differences of the predicted and measured values at three independent datasets

#a: Number of data

	$\Delta\text{TA}^{\#c}$ ($\mu\text{mol/kg}$)	$\Delta\text{DIC}^{\#d}$ ($\mu\text{mol/kg}$)	$\Delta\text{pH25}^{\#e}$
KNOT ($n^{\#a} = 8$) winter	5.6 ± 3.3	2.3 ± 3.4	0.020 ± 0.010
KNOT ($n = 29$) spring	1.0 ± 5.6	-1.3 ± 4.8	0.019 ± 0.016
KNOT ($n = 132$) summer	0.3 ± 6.8	0.1 ± 7.6	0.016 ± 0.022
KNOT ($n = 39$) august	-0.8 ± 6.0	-3.6 ± 8.2	0.022 ± 0.015
KNOT ($n = 208$) total	1.4 ± 5.8	-0.8 ± 7.5	0.017 ± 0.020
Papa ($n = 0$) winter	-	-	-
Papa ($n = 28$) spring	7.2 ± 9.5	4.7 ± 8.0	0.007 ± 0.045
Papa ($n = 17$) summer	2.5 ± 7.8	4.3 ± 8.0	-0.015 ± 0.022
Papa ($n = 27$) august	3.6 ± 7.5	1.6 ± 7.8	0.002 ± 0.020
Papa ($n = 72$) total	4.9 ± 8.5	3.8 ± 8.3	0.000 ± 0.039
OS2013 ($n = 6$)	-1.4 ± 3.6	-4.3 ± 3.6	0.014 ± 0.013
Mean average ($n = 286$)	2.2 ± 6.4	0.3 ± 7.6	0.013 ± 0.024
RMSE ^{#b}	7.4	7.1	0.018

#b: Root mean square error of parameterizations of TA, DIC, and pH25

#c: Difference between TA_{pre} and TA_{mea} values, $\text{TA}_{\text{pre}} - \text{TA}_{\text{mea}}$ #d: Difference between DIC_{pre} and DIC_{mea} values, $\text{DIC}_{\text{pre}} - \text{DIC}_{\text{mea}}$ #e: Difference between pH25_{pre} and pH25_{cal} values, $\text{pH25}_{\text{pre}} - \text{pH25}_{\text{cal}}$

Table 2.4 The average differences between $\Omega_{AR, cal}$ and $\Omega_{AR, pre}$ values at Stations KNOT, K2 and Papa

	$\Delta\Omega_{AR}^{#b}$	
	This study ^{#c}	Kim (2015) ^{#d}
KNOT (n ^{#a} = 208)	0.030 ± 0.045	-0.011 ± 0.067
K2 (n = 103)	0.047 ± 0.042	0.016 ± 0.058
Papa (n = 72)	0.004 ± 0.088	2.205 ± 0.356

#a: Number of data

#b: Difference between $\Omega_{AR, cal}$ and $\Omega_{AR, pre}$ values, $\Omega_{AR, cal} - \Omega_{AR, pre}$

#c: Results from the our sMLR

#d: Results from the rMLR of *Kim et al.*, 2015

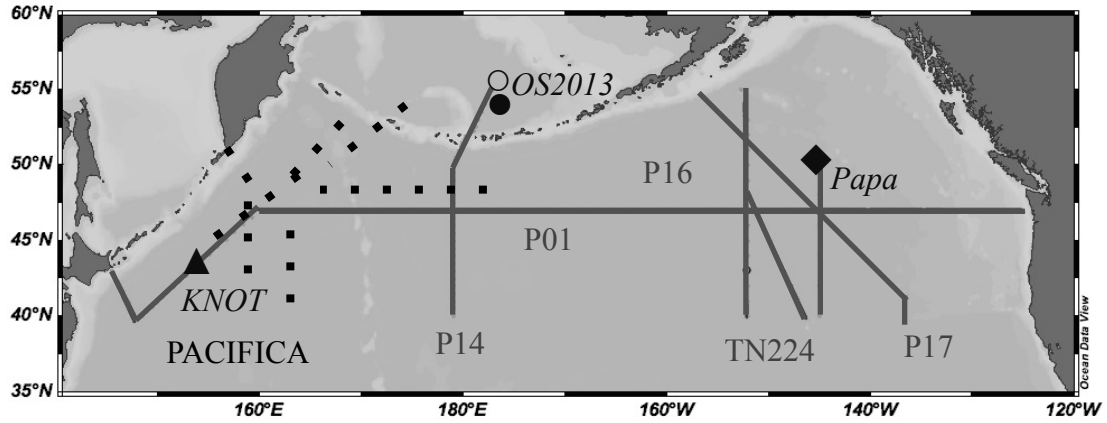


Figure 2.1 Map of hydrographic data locations. Full lines showed the datasets from the CLImate VARIability and predictability (CLIVAR) during the period from 2000 to 2010. The dotted lines showed the datasets from the PACIFic ocean Interior CARbon (PACIFICA) during the period from 2000 to 2010. Independent data used to evaluate the validity of our parameterizations were shown as following: a filled triangle, time series data at Station KNOT (44 °N, 155 °E); a filled diamond, time series data at Station Papa (50 °N, 145 °W); open and filled circles, two data points (OS2013_1 (55 °N, 169 °W) and OS2013_2 (54 °N, 169 °W)) from the cruise of Oshoro–maru during the summer of 2013 (OS2013). We used the Ocean Data View to draw this figure [<http://odv.awi.de>].

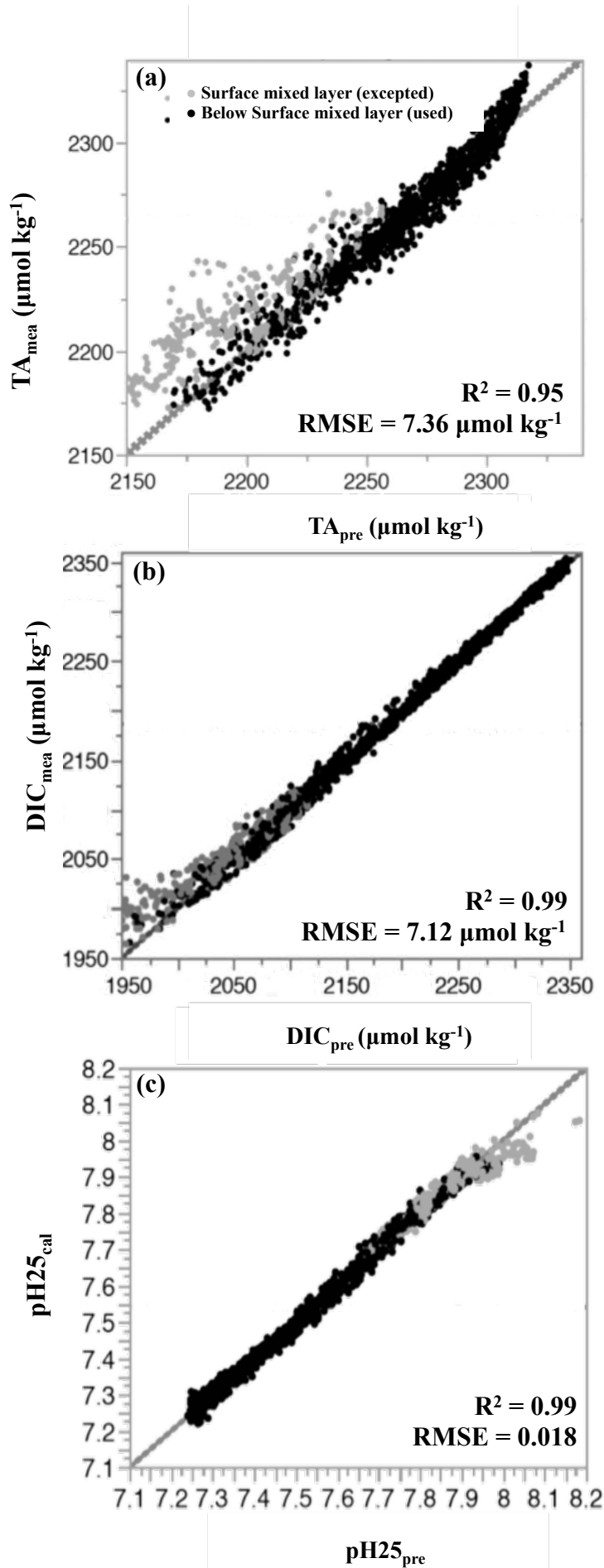


Figure 2.2 Relationships between predicted and measured values of TA, DIC, and pH25 from 40–400 m depth in the North Pacific subpolar region: (a) measured TA (TA_{mea}) ($\mu\text{mol kg}^{-1}$) and predicted TA (TA_{pre}) ($\mu\text{mol kg}^{-1}$); (b) measured DIC (DIC_{mea}) ($\mu\text{mol kg}^{-1}$) and predicted DIC (DIC_{pre}) ($\mu\text{mol kg}^{-1}$); (c) pH25 calculated from TA_{mea} and DIC_{mea} ($pH25_{cal}$) and the pH25 predicted by the parameterization ($pH25_{pre}$). Grey cycles showed the data within the surface mixed layer ($\Delta\sigma_\theta < 0.125$) which had been excepted and black cycles showed the data which had been used in our parameterizations over the depth of 40–400 m (except for the data from the mixed layer).

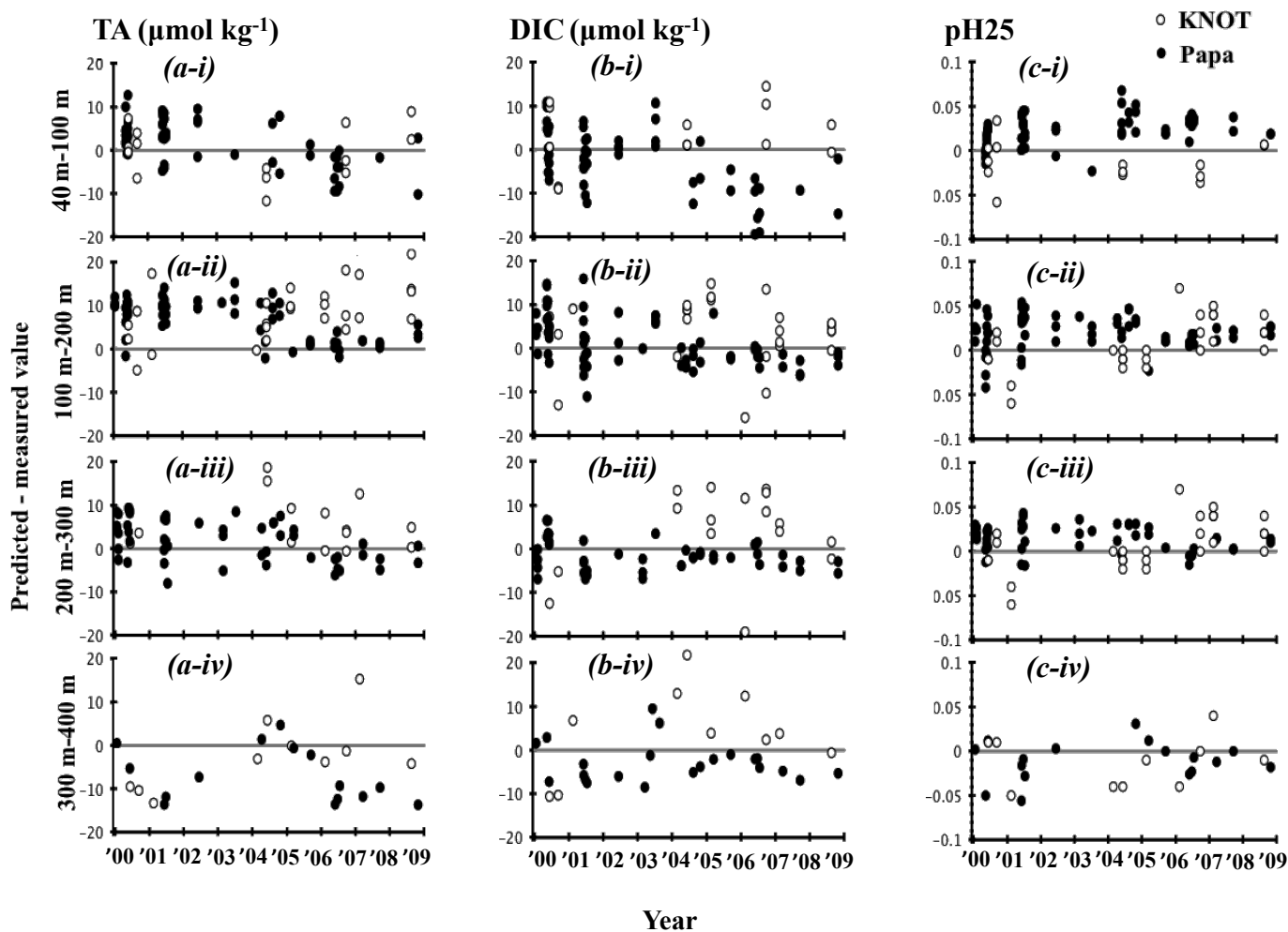


Figure 2.3 Differences in (a) TA, (b) DIC, and (c) pH25 between predicted values and measured values (calculated value for pH25) at Station KNOT (during the period from 2001–2009), Station Papa (during the period from 2001–2009): (i) 40–100 m, (ii) 100–200 m, (iii) 200–300 m and (iv) 300–400 m. Open circles and filled circles were Station KNOT and Papa, respectively. The positive values means that the predicted value is larger than the measured one.

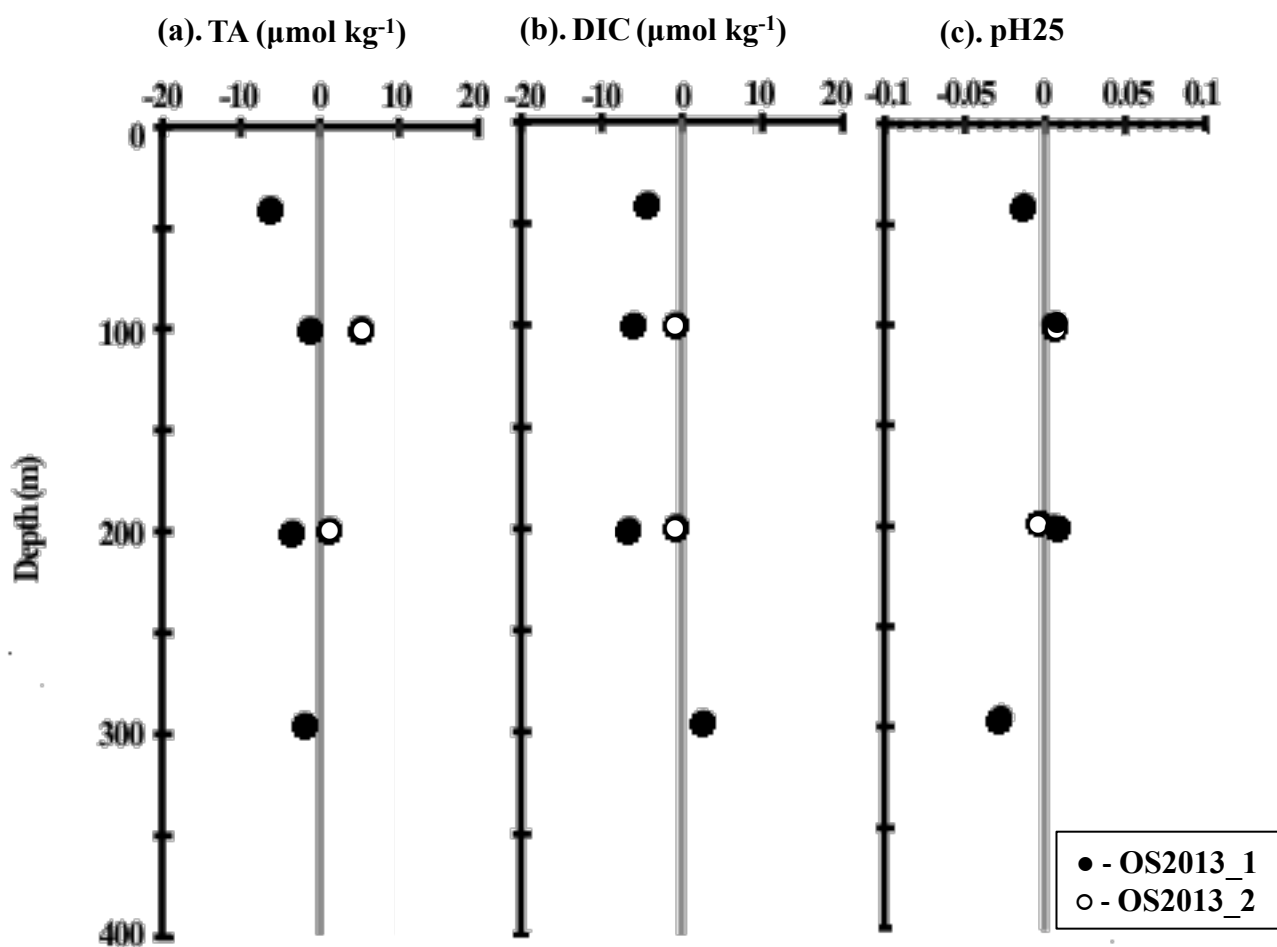


Figure 2.4 Differences in (a) TA, (b) DIC, and (c) pH25 between predicted values and measured values (calculated value for pH25) at the range from the depth below the surface mixed layer to 400 m depth for samples obtained in the North Pacific subpolar region in June 2013. These data were obtained from OS2013_1 (filled circle) and OS2013_2 (open circle). The positive value means that the predicted value is larger than the measured one.

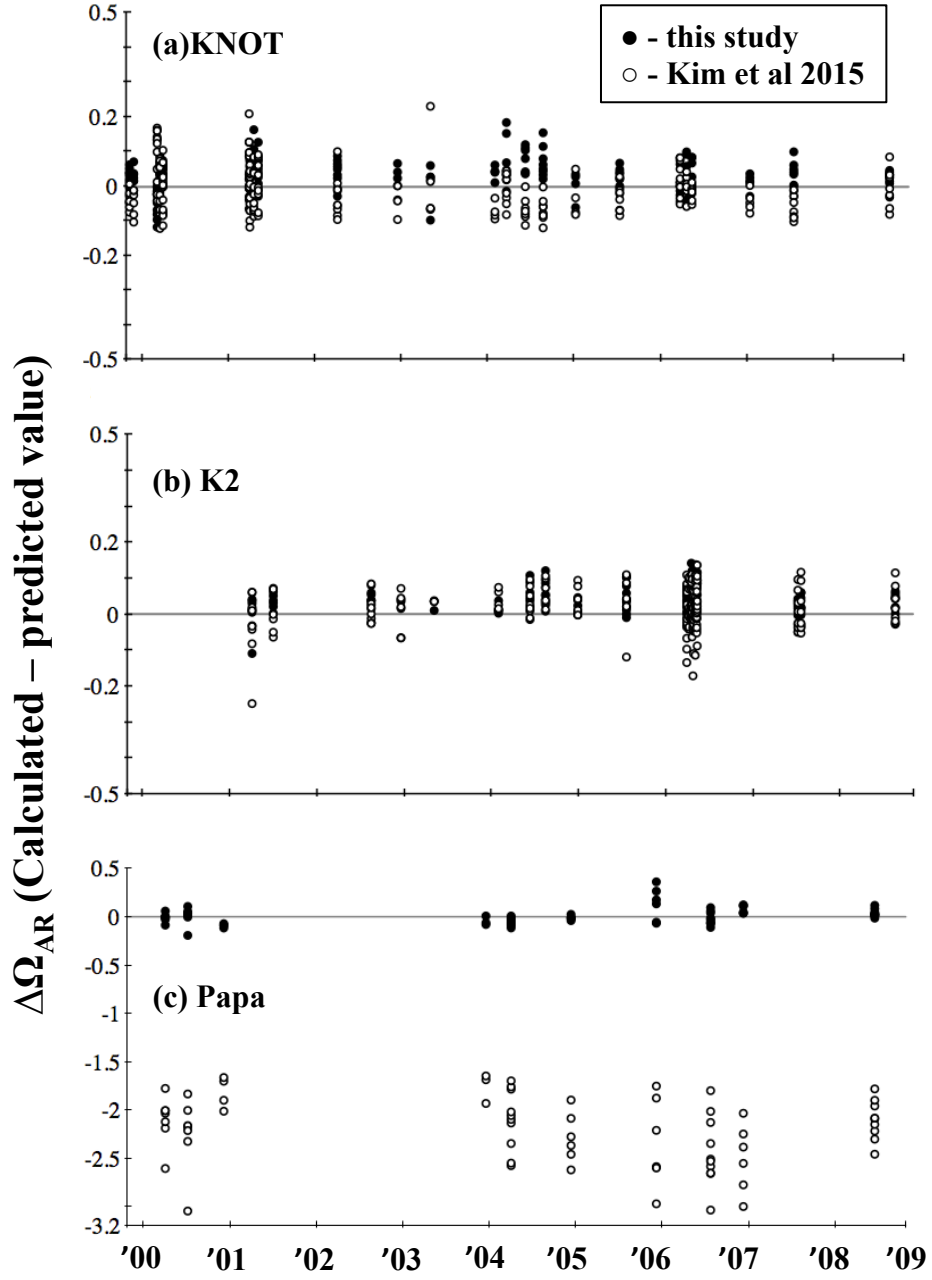


Figure 2.5 Differences in Ω_{AR} between calculated values (calculated from observed TA and DIC) and predicted values (calculated from predicted TA and DIC) at (a) Station KNOT (during the period from 2000 to 2008), (b) Station K2 (during the period from 2000 to 2008) and (c) Station Papa (during the period from 2001 to 2009). Open circles and filled circles were the results from *Kim et al.*, (2015) and this study, respectively. The positive values mean that the calculated value is larger than the predicted one.

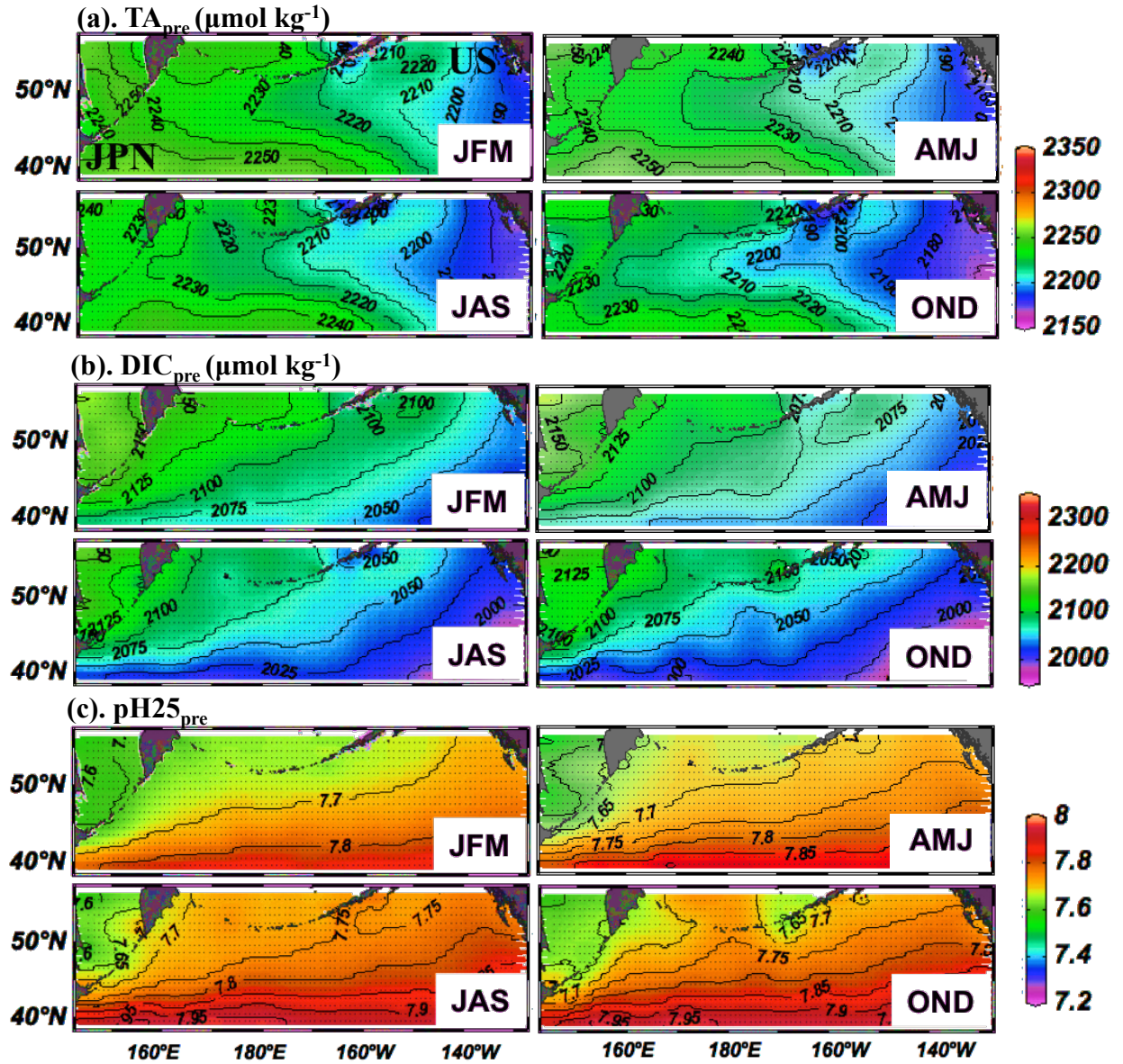


Figure 2.6 Seasonal horizontal distributions of (a) TA_{pre} ($\mu\text{mol kg}^{-1}$, counters every 10 $\mu\text{mol kg}^{-1}$), (b) DIC_{pre} ($\mu\text{mol kg}^{-1}$, counters every 25 $\mu\text{mol kg}^{-1}$), and (c) $pH_{25_{pre}}$ (counters every 0.05 pH) at 50 m over the North Pacific subpolar region for four seasons by applying our parameterizations to the climatological data of DO ($\mu\text{mol kg}^{-1}$), T ($^{\circ}\text{C}$), and S from World Ocean Atlas 2009 (WOA2009). JFM, January, February and March; AMJ, April, May and June; JAS, July, August and September; OND, October, November and December. We used the Ocean Data View to draw these figures [<http://odv.awi.de>].

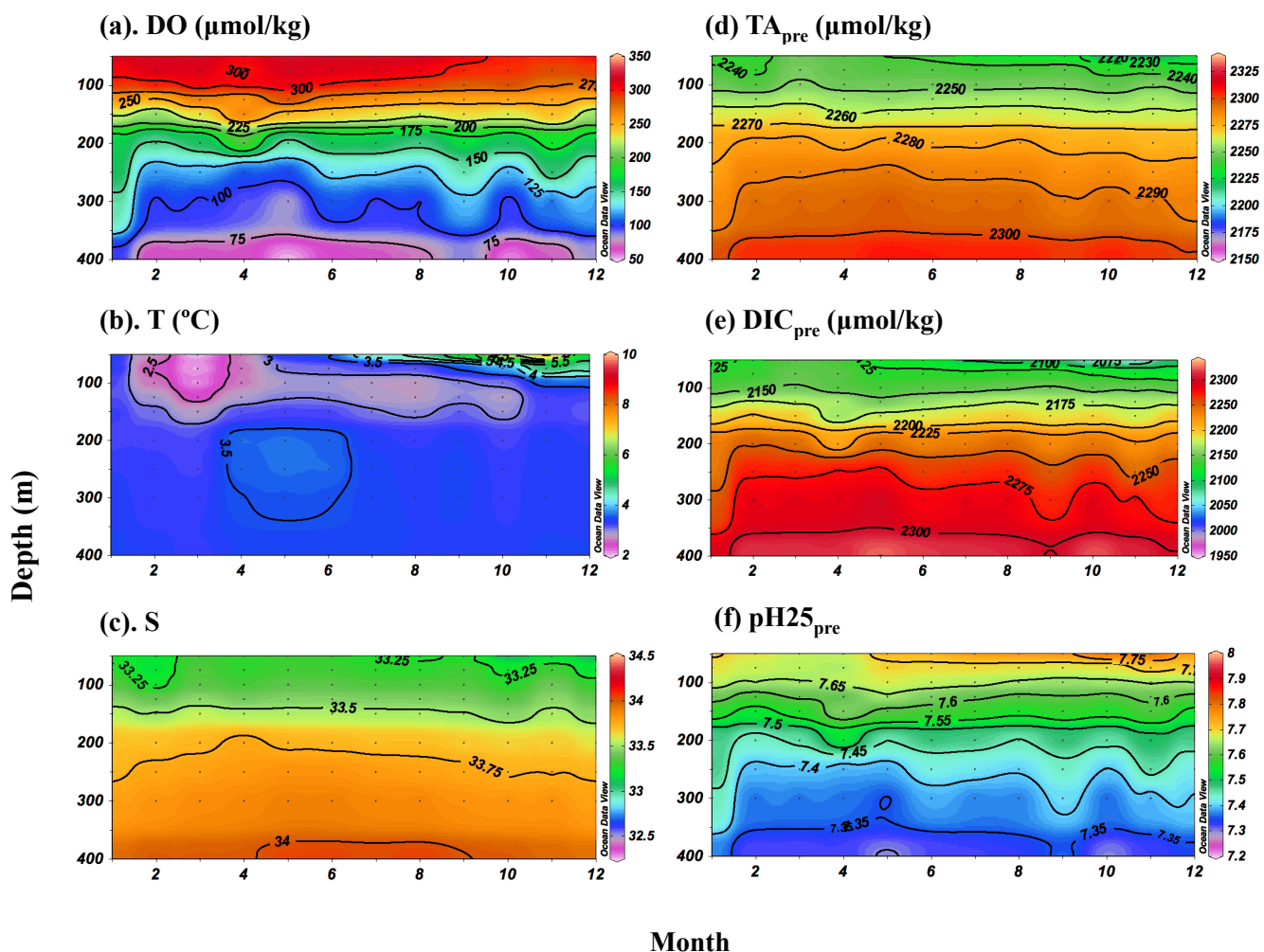


Figure 2.7 Monthly vertical distributions of hydrographic parameters at Station KNOT (44 °N, 155 °E). (a) DO ($\mu\text{mol kg}^{-1}$, counters every 25 $\mu\text{mol kg}^{-1}$), (b) T ($^{\circ}\text{C}$, counters every 0.5 $^{\circ}\text{C}$), and (c) S (kg kg^{-1} , counters every 0.25) from 50 m to 400 m depth of the climatological grid data (44.5 °N, 155.5 °E) of WOA2009. (d) TA_{pre} ($\mu\text{mol kg}^{-1}$, counters every 10 $\mu\text{mol kg}^{-1}$), (e) DIC_{pre} ($\mu\text{mol kg}^{-1}$, counters every 25 $\mu\text{mol kg}^{-1}$), and (f) $\text{pH}_{25_{\text{pre}}}$ (counters every 0.05 pH units) predicted by applying our parameterizations to the above data of DO, T and S. We used the Ocean Data View to draw these figures [<http://odv.awi.de>].

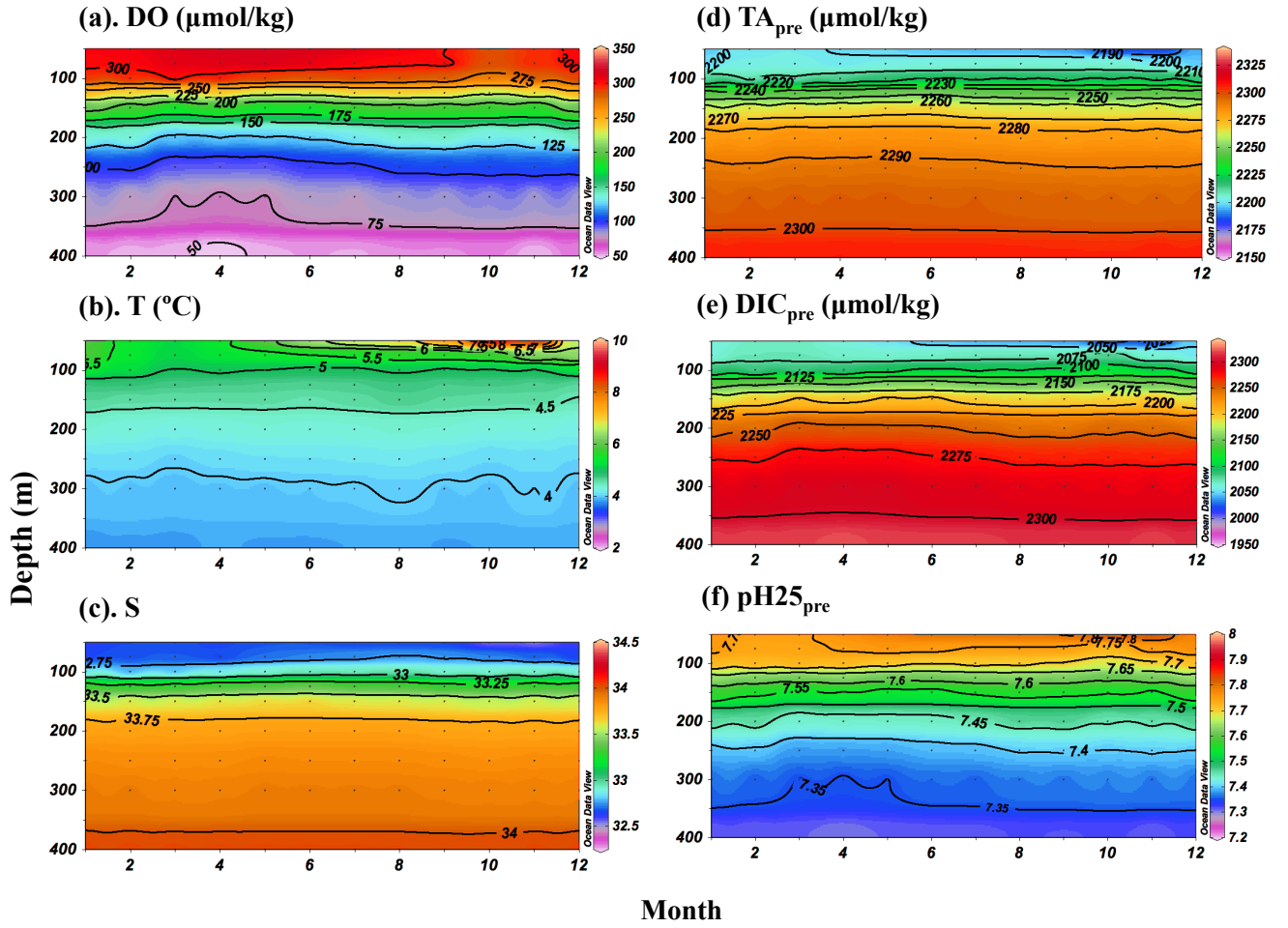


Figure 2.8 Monthly vertical distributions of hydrographic parameters at Station Papa (50 °N, 145 °W). (a) DO ($\mu\text{mol kg}^{-1}$, counters every 25 $\mu\text{mol kg}^{-1}$), (b) T ($^{\circ}\text{C}$, counters every 0.5 $^{\circ}\text{C}$), and (c) S (kg kg^{-1} , counters every 0.25) from 50 m to 400 m depth at the climatological grid data (50.5 °N, 144.5 °W) of WOA2009. (d) TA_{pre} ($\mu\text{mol kg}^{-1}$, counters every 10 $\mu\text{mol kg}^{-1}$), (e) DIC_{pre} ($\mu\text{mol kg}^{-1}$, counters every 25 $\mu\text{mol kg}^{-1}$), and (f) $\text{pH}_{25_{\text{pre}}}$ (counters every 0.05 pH units) predicted by applying our parameterizations to the above data of DO, T, and S. We used the Ocean Data View to draw these figures [<http://odv.awi.de>].

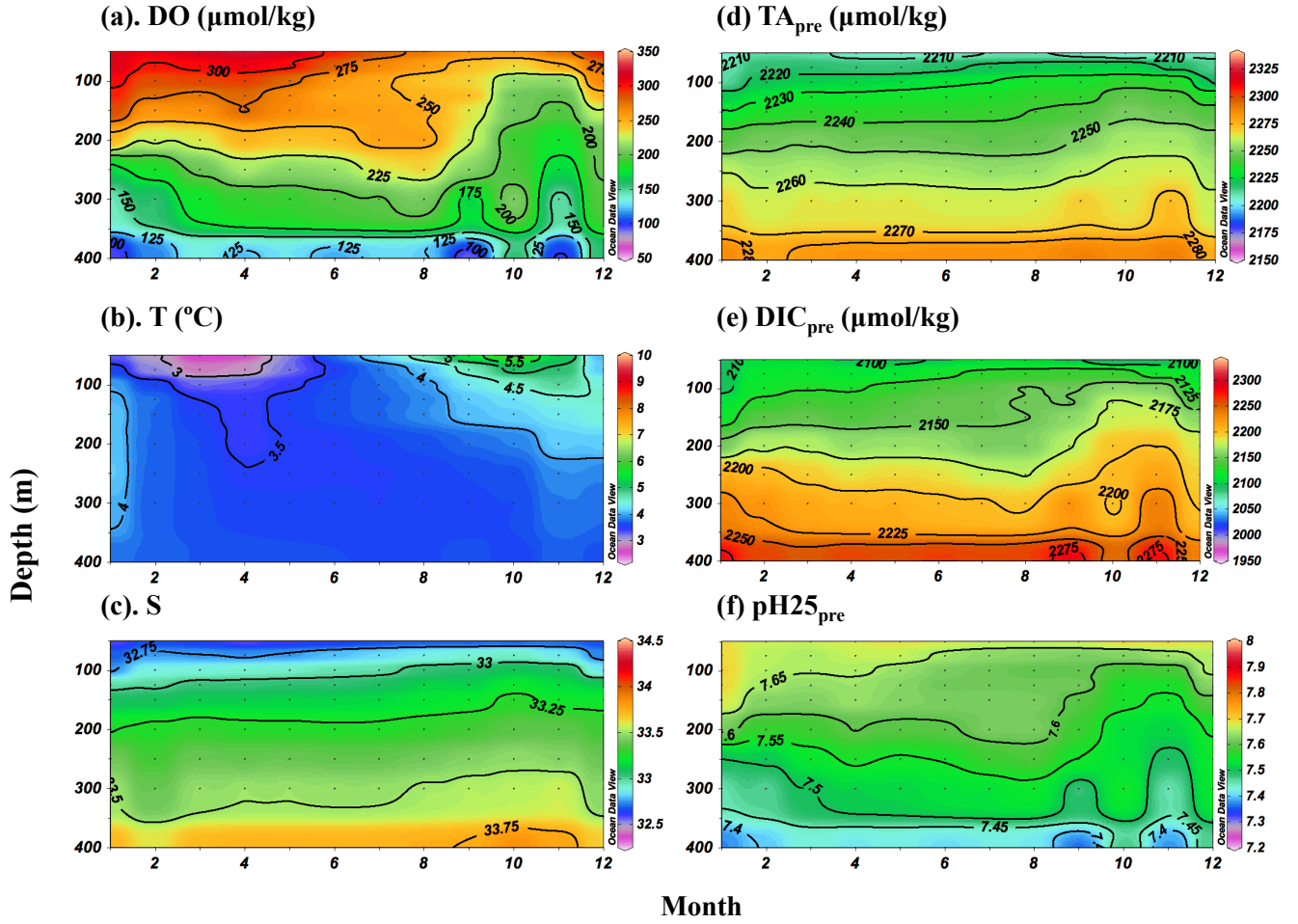
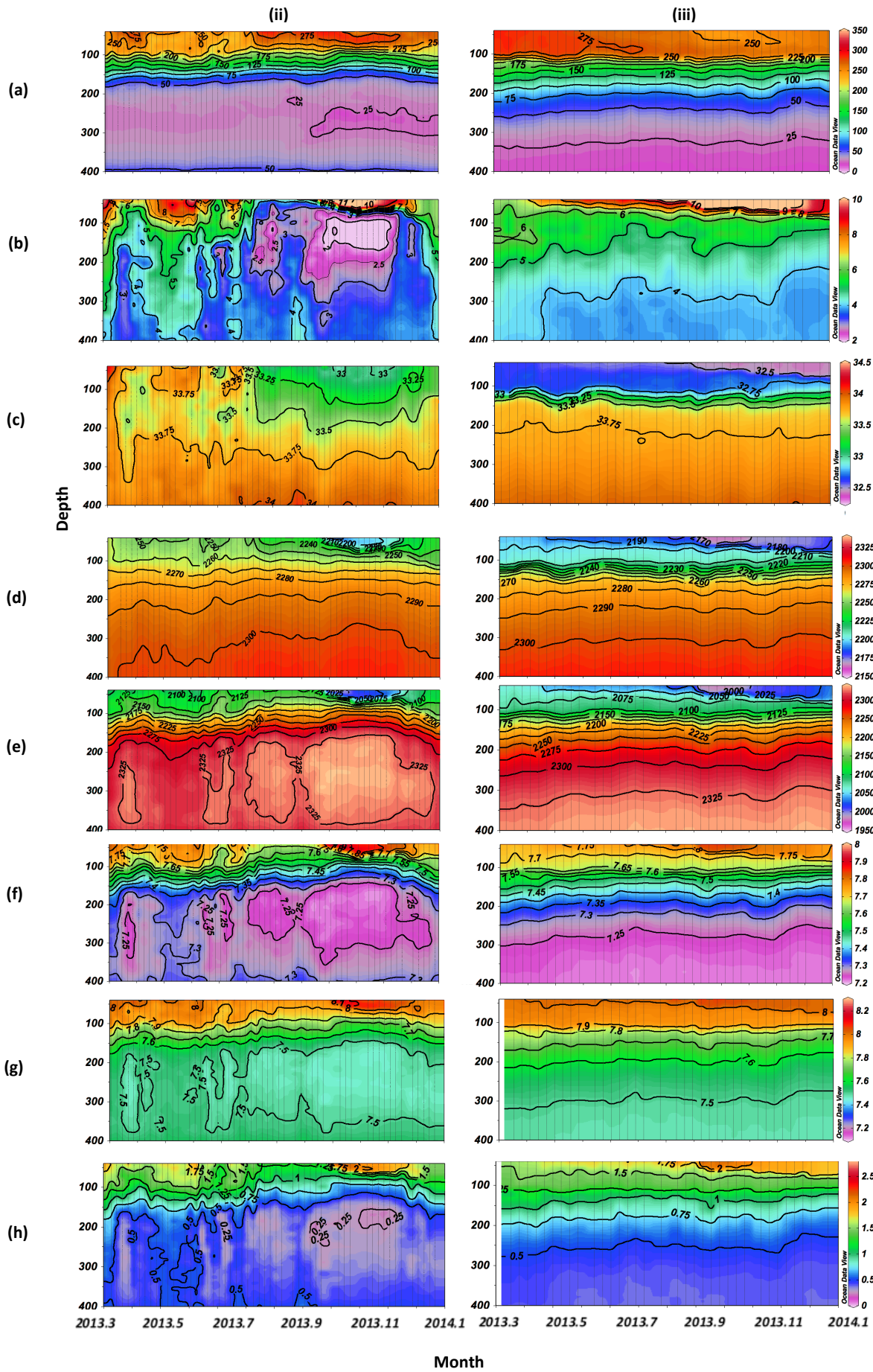


Figure 2.9 Monthly vertical distributions of hydrographic parameters at OS2013_1 (55°N, 169°W). (a) DO ($\mu\text{mol kg}^{-1}$, counters every 25 $\mu\text{mol kg}^{-1}$), (b) T ($^{\circ}\text{C}$, counters every 0.5 $^{\circ}\text{C}$), and (c) S (kg kg^{-1} , counters every 0.25) from 50 m to 400 m depth at the climatological grid data (55.5°N, 168.5°W) of WOA2009. (d) TA_{pre} ($\mu\text{mol kg}^{-1}$, counters every 10 $\mu\text{mol kg}^{-1}$), (e) DIC_{pre} ($\mu\text{mol kg}^{-1}$, counters every 25 $\mu\text{mol kg}^{-1}$), and (f) $\text{pH}_{25_{\text{pre}}}$ (counters every 0.05 pH units) predicted by applying our parameterizations to the above data of DO, T and S. We used the Ocean Data View to draw these figures [<http://odv.awi.de>].



(Continued)

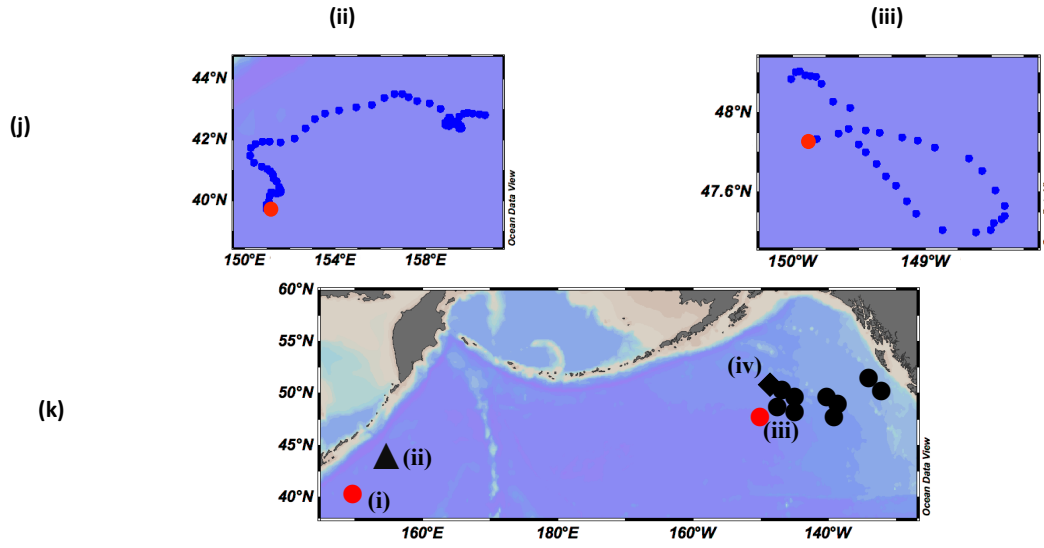


Figure 2.10 Time-series of vertical distributions of (d) TA_{pre} ($\mu \text{ mol kg}^{-1}$, counters every $10 \mu \text{ mol kg}^{-1}$), (e) DIC_{pre} ($\mu \text{ mol g}^{-1}$, counters every $25 \mu \text{ mol kg}^{-1}$), (f) $\text{pH}_{25_{\text{pre}}}$ (counters every 0.05 pH units), (g) $\text{pH}_{\text{in situ, pre}}$ (counters every 0.05 pH units), and (h) $\Omega_{\text{AR, pre}}$ by applying our parameterizations to the dataset of (a) DO ($\mu \text{ mol kg}^{-1}$, counters every $25 \mu \text{ mol kg}^{-1}$), (b) T ($^{\circ}\text{C}$, counters every $0.5 ^{\circ}\text{C}$), and (c) S (kg kg^{-1} , counters every 0.25) of Argo profiling floats from 40 m to 400 m depth during the period of March 2013 to January 2014 in the North Pacific subpolar region. Maps showed the (h) trajectories and (j) locations of Argo profiling floats distributed in the North Pacific subpolar region. (i) and (iii) showed the Argo floats in the western side and eastern side of the North Pacific subpolar region (WMO codes of 5904028 and 5904106, respectively). In (a)–(g), dots showed the sampling points. In (j), blue points showed the trajectories of Argo profiling floats and red points showed the ending of the trajectories. In (k), the filled triangle and diamond showed the time series data at Station KNOT and Papa, the red filled cycles showed the positions of Argo profiling floats used in (i) and (iii) and the black filled cycles showed the positions of floats unused in this figure (all of the filled cycles showed the last position of the trajectories before January, 30th, 2014). We used the Ocean Data View to draw these figures [<http://odv.awi.de>].

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Chapter 3

Quasi-real-time and high-resolution spatiotemporal distribution of ocean anthropogenic CO₂

3.1 Introduction

There is currently great interest in understanding the global carbon cycle because of the greenhouse effect of CO₂ on Earth's climate. Since the 1750s, the ocean has played an important role as a sink of anthropogenic CO₂, absorbing almost one-fourth of the CO₂ released by anthropogenic activities [Le Quere *et al.*, 2014]. The increasing absorption of anthropogenic CO₂ by the ocean has critically affected marine organisms by causing ocean acidification and reducing the ocean's buffering capacity [Doney *et al.*, 2009].

To understand carbon chemistry changes in the ocean, oceanographers have collected high-precision carbon chemistry data, including total alkalinity (TA, 0.1%), dissolved inorganic carbon (DIC, 0.1%), and pH (0.1%), throughout the global ocean from the sea surface to the bottom waters with decadal-scale temporal resolution since the last several decades of the 20th century [Suzuki *et al.*, 2013]. Those data, however, were collected mainly during research cruises, and ship-based data cannot provide information on annual, seasonal, and monthly variability; and their spatial resolution (distance between observation stations) is only 2–5° of latitude and longitude, about 100–500 km [Suzuki *et al.*, 2013]. In addition, time-series observations of long-term oceanic CO₂ variations made at stationary ocean observation stations are available, in some representative regions (e.g., ocean stations ALOHA, Papa, and KNOT in the North Pacific; BATS in the North Atlantic), but time-series observations in the global ocean are spatially sparse (CDIAC). To overcome the limited availability and spatiotemporal resolution of observational carbon chemistry data, researchers have developed parameterizations and models of oceanic CO₂ to complement the observational data. These parameterizations and models use other hydrographical properties, including dissolved oxygen (DO),

temperature (T), salinity (S), chlorophyll-*a* (Chl) and nitrate (NO₃⁻), which have been measured with higher spatial and temporal resolutions than the carbon chemistry data, to clarify spatiotemporal changes of carbon chemistry in the ocean [Juranek *et al.*, 2011].

From 2000, ‘automatic measurement robots’ - Argo profiling floats are deployed in the global ocean to monitor large and long-term scale oceanic changes on the basis of Argo program (Argo Steering Team). The Argo float can measure on physical parameter of T and S from sea surface to a depth of 2000 m every 5-10 days [Thierry *et al.*, 2015]. Now over 3000 of the Argo floats are active and deliver well quality controlled data with high accuracy and horizontal/vertical resolution in real-time, which makes it possible to analyze more accurate basin scale oceanic changes than before (Argo Steering Team) [Thierry *et al.*, 2015]. Further, recent development of biogeochemical sensor technology, Biogeochemical Argo float (BGC Argo), which is equipped with DO, NO₃⁻ or Chl sensor, had been started to deploy in the global ocean (Biogeochemical-Argo Task Team). Although the BGC Argo project had been started to construct a global array, the number of profile data of Argo floats with DO sensor (DO-Argo) is still 8% of total, and those quality control are not fully conducted yet and not enough accuracy because of complex procedure [Thierry *et al.*, 2016][Takeshita *et al.*, 2013]. They are the main reasons why the use of DO-Argo data is still limited especially for some pilot studies (e.g., physical properties for eddies, mixed layer depth and ocean circulations, and biological properties for net production [Inoue and Kouketsu, 2015; Riser and Johnson, 2008] [Sukigara *et al.*, 2012], there is a large possibility to understand oceanic carbon chemistry process by overcoming the negative situations.

To obtain an oceanic carbon chemistry dataset with the same spatiotemporal scale as the Argo physical and biological datasets, parameterization techniques have been applied to the high-resolution physical and biological Argo datasets [Juranek *et al.*, 2011; Li *et al.*, 2016; Williams *et al.*, 2015]. Simple, high-precision parameterizations of oceanic TA, DIC, and pH have previously been applied to DO, T, and S observational data collected by Argo profiling floats in the subarctic North Pacific and

used to produce quasi-real-time high-resolution maps of the vertical distributions of carbon chemistry to 400 m depth (see details in Chapter 2) [Li *et al.*, 2016]. Moreover, North Pacific Intermediate Water, which is produced in the western subarctic North Pacific, affects climate and marine circulation of the entire North Pacific Ocean [Ueno, 2003; Yasuda, 1997]. Further, recent studies have shown strengthening ocean stratification in the subarctic North Pacific [Watanabe *et al.*, 2001], which is expected to decrease both biological productivity and the ocean's capacity to buffer anthropogenic CO₂ [Doney *et al.*, 2009]. Therefore, we chose this region to test new parameterizations of oceanic carbon chemistry and their application to hydrographical data with high spatiotemporal resolution obtained from Argo profiling floats. Then, using these reconstructed TA and DIC values and oceanic carbon chemistry thermodynamics, we calculated the quasi-real-time distribution of anthropogenic CO₂ (C_{ant}) at high-resolution in the subarctic North Pacific and examined the changes in C_{ant} in this region over the last several decades.

3.2 Improved parameterizations of TA, DIC and pH

3.2.1 Parameterizations of TA, DIC and pH from surface to 2000 m depth

A previous study (see details in Chapter 2) provided parameterizations for TA, DIC, and pH from 40 to 400 m depth in the subarctic North Pacific. By the 1990s, C_{ant} had penetrated as deep as about 1500 m in the subarctic North Pacific [Sabine *et al.*, 2004]. According to the penetration rate of C_{ant} , it is necessary to consider parameterizations of the ocean carbon chemistry by to 2000 m depth in this region to examine how the distribution of C_{ant} has changed. BGC Argo profiling floats measure hydrographical data such as DO, T, and S data from a depth of 2000 m [Thierry, *et al.*, 2015, Thierry, *et al.*, 2016]. Because pressure (P) is one of the main factors affecting the dissociation constants of carbonic acid and the dissolution of calcium carbonate in the ocean, we provided new parameterizations for TA, DIC, and pH to 2000 m depth covering most of the subarctic North Pacific (40°N–56°N, 145°E–130°W, Fig. 3.1) that also take account of P as follows:

$$TA_{pre} = 486.3 - 0.1031 DO - 4.992 T + 54.03 S + 0.04155 P \quad (3.1)$$

$$(n = 3956, R^2 = 0.98, RMSE = 8.2 \mu\text{mol kg}^{-1})$$

$$DIC_{pre} = 963.5 - 0.6485 DO - 17.39 T + 42.7 S + 0.009313 P \quad (3.2)$$

$$(n = 4004, R^2 = 0.99, RMSE = 5.6 \mu\text{mol kg}^{-1})$$

$$pH_{pre} = 6.455 + 0.001607 DO + 0.03418 T + 0.01758 S + 5.877 \times 10^{-5} P \quad (3.3)$$

$$(n = 3803, R^2 = 0.99, RMSE = 0.020)$$

where TA_{pre} and DIC_{pre} are the predicted values of TA and DIC, pH_{pre} is the predicted pH at 25 °C on the seawater scale, and the units of DO, T, S and P are $\mu\text{mol kg}^{-1}$, °C, dimensionless, and dbar, respectively. Here, R^2 and RMSE represent the coefficient of determination and the root mean square

error, respectively. Because DO, T, S and P have *F-values* of more than 2.4 (Table 3.1, Fig.3.2), we can use the DO, T, S, and P values to reconstruct TA, DIC, and pH to 2000 m depth over the subarctic North Pacific. These relationships are consistent with their parameterizations to 400 m depth used to reconstruct oceanic carbon chemistry at weekly to decadal scales [Li *et al.*, 2016].

Eqs. (3.1) - (3.3) were obtained by using observed high-precision carbon chemistry and hydrographic datasets for DO, T, S, and P collected by the CLImate VARIability and predictability (CLIVAR, available from the Carbon Dioxide Information Analysis Center; <http://cdiac.ornl.gov/oceans>) and PACIFic ocean Interior Carbon (PACIFICA, available from PACIFICA Database; <https://www.nodc.noaa.gov/ocads/oceans/PACIFICA/>) international programs from 2000 to 2010 (Fig. 3.1). The data quality after 2000 was controlled by using Certified Referenced Materials distributed by A.G. Dickson of the Scripps Institution of Oceanography.

3.2.2 Differences in TA and DIC between observations and parameterizations

To validate our parameterizations, we compared the predicted values of TA and DIC with measured values derived from two independent datasets collected at observational time-series stations KNOT (44°N, 155°E) in the western and Papa (50°N, 145°W) in the eastern subarctic North Pacific (these data were obtained from the Carbon Dioxide Information Analysis Center; <http://cdiac.ornl.gov/oceans>). The differences between measured and predicted values for both TA and DIC were mostly within 10 $\mu\text{mol kg}^{-1}$ and consistent with previously reported weekly-to-decadal scale results (Fig. 2.3 and Fig 3.3).

3.3 Estimation of C_{ant} using Argo-based DO, T, and S data

3.3.1 Hydrographical data from Argo profiling floats in the subarctic North Pacific applied to equations (3.1) and (3.2)

DO-Argos were operated mostly in the western and eastern parts of the subarctic North Pacific (Fig. 3.7(g)). Argo DO data can be validated by comparing them with discrete DO observation data obtained from bottle samples collected near DO-Argo. In this region, the number of bottle data is not enough and too shallow to validate all of the Argo DO data in this region. Therefore, we chose and tested two of DO-Argo floats (WMO ID: 2900540, during 2005–2008 (west DO-Argo) and 5904106, during 2013–2016 (east DO-Argo)). These Argo float data and metadata are available from the Argo Global Data Assembly Centre (snapshot on 8 December 2016; SEANOE, <http://doi.org/10.17882/42182#47075>). West DO-Argo in the western subarctic North Pacific, which is operated by the Japan Agency for Marine-Earth Science and Technology, drifts at a parking depth of 1000 dbar and collects ascending profile data from 2000 dbar to the surface every 10 days. East DO-Argo in the eastern subarctic North Pacific, which is operated by the Teledyne Webb Research Corporation, also drifts at a parking depth of 1000 dbar, and it collects ascending profile data from 2000 dbar to the surface every 7 days. We used the linear relationship between the Argo DO data and bottle DO data collected near these Argo floats to correct Argo DO data (details in section 3.3.3).

3.3.2 Application of parameterizations and Argo-based DO, T, and S data to the estimation of the anthropogenic DIC (C_{ant}) and disequilibrium DIC (C_{diseq})

According to the concepts outlined in *Gruber and Sarmiento* [2006], the sum of the anthropogenic DIC (C_{ant}) and disequilibrium DIC (C_{diseq}) (C_{res}) can be written as

$$C_{\text{res}} = C_{\text{ant}} + C_{\text{diseq}} = \text{DIC} - C_{\text{pi, sat}} - C_{\text{soft}} - C_{\text{carb}} \quad (3.4)$$

where $C_{\text{pi, sat}}$ (preindustrial saturated DIC) and C_{res} are preformed components and C_{soft} , which is derived from the remineralization of organic matter, and C_{carb} , which is derived from the dissolution of CaCO_3 (see below), are regenerated components. In this study, we used the predicted DIC (DIC_{pre}) calculated with Eq. (3.2) instead of the observed DIC. For the parameterization of DIC_{pre} , we used observed DIC data from the 2000s, which were influenced by both an anthropogenic component derived from the increasing level of anthropogenic CO_2 and a non-anthropogenic component derived from changes in DO, T, S, and P; thus, DIC_{pre} consists of C_{ant} from the 2000s and non-anthropogenic DIC at an arbitrary time. Here, we assumed that the C_{ant} component of DIC_{pre} was constant at the C_{ant} value in 2005, determined by calculating the average C_{ant} value during 2000–2010.

$C_{\text{pi, sat}}$ can be calculated from the equilibrium carbon chemistry relationships as follows:

$$C_{\text{pi, sat}} = f(\text{TA}_0, \text{pCO}_2 = 280 \text{ ppm}, T, S, P) \quad (3.5)$$

where TA_0 is preformed TA from the surface ocean obtained from the linear relationship between TA_0 and salinity ($\text{TA}_0 = 399 + 54.629S$) [Millero *et al.*, 1998]. We calculated the contribution of remineralization of organic matter to DIC as

$$C_{\text{soft}} = 117/170 \text{ AOU} \quad (3.6)$$

where 117/170 is the Redfield ratio of carbon to oxygen applied by *Anderson and Sarmiento* [1994] and AOU is apparent oxygen utilization. AOU is calculated as the difference between saturated DO and observed DO. Here, we assumed that the Redfield ratio of carbon to oxygen was constant vertically and used the N : C : O_2 ratio of 16 : 117 : (– 170) [Anderson and Sarmiento, 1994]. We calculated the contribution from the dissolution of CaCO_3 as follows:

$$C_{\text{carb}} = 0.5 (TA_{\text{pre}} - TA_0 - 16/170 \text{ AOU}) \quad (3.7)$$

where 16:170 is the Redfield ratio of nitrogen to oxygen applied by *Anderson and Sarmiento* [1994]. The term 16/170AOU corrects the calculation for the fact that TA also includes nitrate formed by the remineralization of organic matter. The coefficient 0.5 indicates that a change of one mole in TA corresponds to a change of one-half mole in DIC.

We did not use the traditional method to calculate the disequilibrium DIC in seawater [*Gruber et al.*, 1996], because we did not have any seawater age information. Therefore, assuming that the CO₂ disequilibrium value would be constant from the surface mixed layer to the ocean interior, we estimated the CO₂ disequilibrium value at the mixed layer depth (MLD) ($C_{\text{diseq, MLD}}$) by subtracting the preformed and regenerated components at the MLD (saturated DIC at MLD ($C_{\text{sat, MLD}}$) and C_{soft} and C_{carb} at MLD ($C_{\text{carb, MLD}}$ and $C_{\text{carb, MLD}}$), respectively) from DIC_{pre} at the MLD (DIC_{pre MLD}).

$C_{\text{diseq, MLD}}$ in 2005 was calculated as follows:

$$C_{\text{sat, MLD}} = f(TA_0, pCO_2 = 375 \text{ ppm}, T, S, P) \quad (3.8)$$

$$C_{\text{diseq, MLD}} = \text{DIC}_{\text{pre, MLD}} - C_{\text{sat, MLD}} - C_{\text{soft, MLD}} - C_{\text{carb, MLD}} \quad (3.9)$$

Because the DIC_{pre} value in 2005 included C_{ant} , we here used the 2005 pCO₂ value (375 ppm) in Eq. (3.8). We used the mean values of $C_{\text{diseq, MLD}}$ of each Argo float as C_{diseq} for all periods of that float. C_{diseq} was $-9.2 \text{ } \mu\text{mol kg}^{-1}$ for float 2900540 and $-5.1 \text{ } \mu\text{mol kg}^{-1}$ for float 5904106, and C_{diseq} calculated by the traditional method in the previous study of the North Pacific was $-13 \pm 5 \text{ } \mu\text{mol kg}^{-1}$ [*Gruber et al.*, 1996]. Finally, we estimated C_{ant} with Eq. (3.10):

$$C_{\text{ant}} = C_{\text{res}} - C_{\text{diseq}} \quad (3.10).$$

3.3.1 Calibration of Argo-based dissolved oxygen data

The Argo DO data that we used in this study were measured by Seabird SBE43F (2900540) and Aanderaa 4330 optode (5904106) floats, respectively. Although data management procedure for DO data has been decided by Argo data management team, quality control of those data delivered from the Global Argo Data Assembly Center are not properly implemented. Since the above DO data possibly include some biases or errors, original quality controls must be needed. Therefore, to assess the accuracy of the Argo DO data, we compared Argo S and DO profiles with observed S and DO profiles based on discrete bottle samples (Fig. 3.5). The bottle DO data used to calibrate 2900540 were collected at 165.1°E, 40.9°N on 17 June 2006 during cruise RF-06-0, and those used to calibrate 5904106 were collected at 145.8°W, 48.1°N on 11 June 2015 during cruise P16N.2 (these data are available from the CLIVAR & Carbon Hydrographic Data Office; <https://cchdo.ucsd.edu/>). For Argo DO data, we chose two stations from 2900540 at 164.2°E, 41.9°N, 166.9°E, 41.5°N, and three stations from 5904106 at 145.8°W, 48.1°N, 146.5°W, 48.1°N and 144.2°W, 48.7°N within the same season of bottle DO data. We corrected the Argo DO data from 40 to 2000 m depth by using the linear relationships between bottle DO data and Argo 2900540 ($R^2 = 0.98$, $\text{RMSE} = 10.9 \mu\text{mol kg}^{-1}$, $n = 14$) and 5904106 ($R^2 = 0.99$, $\text{RMSE} = 10.7 \mu\text{mol kg}^{-1}$, $n = 25$) data (Fig. 3.5). For 2900540, the propagated uncertainty from the RMSE of $\pm 10.9 \mu\text{mol kg}^{-1}$ equates to an error of $\pm 1.3 \mu\text{mol kg}^{-1}$ and $\pm 6.5 \mu\text{mol kg}^{-1}$ in TA_{pre} and DIC_{pre} , respectively. For 5904106, the propagated uncertainty from the RMSE of $\pm 10.7 \mu\text{mol kg}^{-1}$ equates to an error of $\pm 1.3 \mu\text{mol kg}^{-1}$ and $\pm 6.4 \mu\text{mol kg}^{-1}$ in TA_{pre} and DIC_{pre} , respectively. The uncertainty from the average RMSE of Argo DO $\pm 10.8 \mu\text{mol kg}^{-1}$ also caused an error of $\pm 14.6 \mu\text{mol kg}^{-1}$ in the estimation of C_{ant} .

3.4 High-resolution distributions of carbon species and C_{ant}

We applied our new TA and DIC parameterizations to DO, T, S, and P of BGC Argo datasets collected from the previous two gyres (Fig. 3.6) and showed that the vertical distributions of TA_{pre} and DIC_{pre} varied over a wider range and changed more smoothly in the east than in the west. These results are mostly consistent with previous findings [Li *et al.*, 2016].

Then, we first used the predicted DIC and TA values to calculate C_{ant} , C_{diseq} and C_{res} by from Argo DO, T, S, and P data over the subarctic North Pacific (Fig. 3.7). Here, the C_{res} and C_{ant} represent the anthropogenic injection CO_2 to the ocean until 2005 as an average from 2000 to 2010.

We had no data on seawater age, so we could not use the traditional method of estimating C_{diseq} due to disequilibrium in the air–sea exchange [Gruber *et al.*, 1996]. Instead, we assumed that the C_{diseq} would be constant vertically from the surface mixed layer and subtracted the preformed and regenerated components from DIC_{pre} at the mixed layer depth (MLD) ($C_{\text{diseq, MLD}}$) as the C_{diseq} value. We used the mean $C_{\text{diseq, MLD}}$ value of each Argo float as C_{diseq} for all periods. The $C_{\text{diseq, MLD}}$ for west and east DO-Argo were $-9.2 \mu\text{mol kg}^{-1}$ and $-5.1 \mu\text{mol kg}^{-1}$, respectively, which were corresponding to the order of $-13 \pm 5 \mu\text{mol kg}^{-1}$ [Gruber *et al.*, 1996] calculated by the traditional method. Most $C_{\text{diseq, MLD}}$ values were negative because they represented an air–sea CO_2 exchange period of about half of a year (Fig. 3.7). However, some positive $C_{\text{diseq, MLD}}$ values appeared in the summer (April–June; (Fig. 3.7a, d) for both the Argo floats. This result indicates that a shallower MLD may facilitate the air–sea exchange of CO_2 , making it temporarily easier to reach equilibrium.

In the subarctic North Pacific, C_{ant} thus reached depths of 1700–1900 m, about 300 m deeper than the C_{ant} in the 1990s (Fig. 3.7) [Sabine *et al.*, 2004, 2008]. In the west, C_{ant} penetrated more deeply than in the east and was relatively high; this result is consistent with the isopycnal distribution of C_{ant} calculated by a previous global-scale study²⁰. In addition, west DO-Argo drifts at relatively low latitudes and therefore has a lower buffering factor than east DO-Argo, which drifts at higher latitudes. The average C_{ant} inventories of west and east DO-Argo were 32.3 and 17.3 mol m^{-2} ,

respectively. The average inventory of C_{ant} in the subarctic North Pacific to 2000 m depth was therefore $24.8 \pm 10.2 \text{ mol m}^{-2}$, about 20% higher than the average during the 1990s [Sabine *et al.*, 2004]. The rate of ocean uptake of CO_2 was $0.5 \text{ mol m}^{-2} \text{ y}^{-1}$ in this region, a relatively low value for the North Pacific [Sabine *et al.*, 2008]. This low value may reflect a strengthening of ocean stratification in the subarctic North Pacific [Watanabe *et al.*, 2001].

By using BGC Argo or other automatic sensor datasets of DO, T, S, and P, our parameterizations can allow us to give strong evidence of detailed spatiotemporal distributions on ocean carbon chemistry and anthropogenic CO_2 above 2000 m depth in quasi-real time over the subarctic North Pacific which a traditional ship-based method cannot achieve. In the future, application of our parameterization method to BGC Argo data from the global ocean should make it possible to obtain a high-resolution map and detailed time-series distribution of global oceanic CO_2 cycle parameters.

Table

Table 3.1 Summaries of our parameterizations for the TA, DIC, and pH in the North Pacific subarctic region.

	TA (n ^{#c} = 3956)			DIC (n = 4004)			pH		
	R ² ^{#d}	RMSE ^{#e}	F ^{#f}	R ²	RMSE	F	R ²	RMSE	F
DO ^{#a}			1394			118721			54686
T ^{#b}			2762			72074			21909
S ^{#a}	0.98	8.18	5414	0.99	5.60	7228	0.99	0.20	93
P ^{#b}			7935			855			2608

#a: Value derived from the discrete Niskin bottles

#b: Value derived from the CTD sensor

#c: Numbers of data

#d: Coefficient of determination

#e: Root mean square error

#f: Value from *F*-test

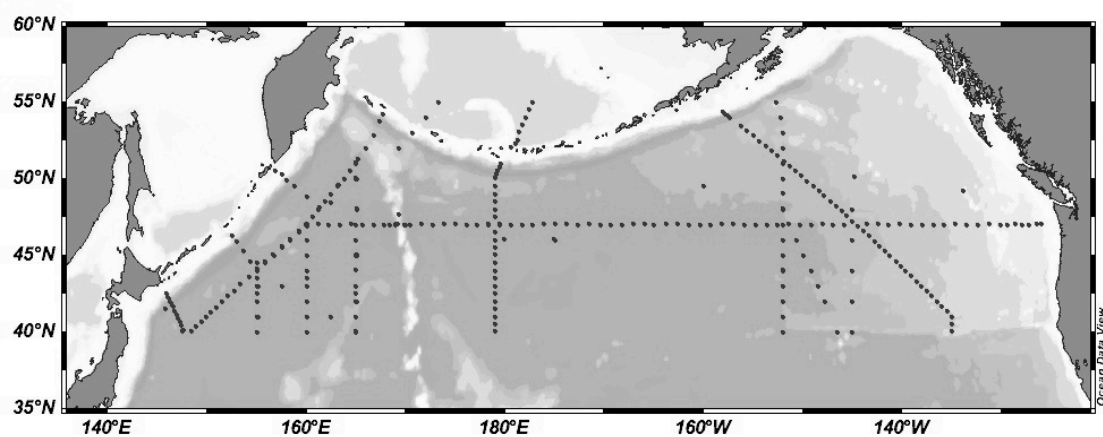


Figure 3.1

Map of the CLIVAR (CLImate VARIability and predictability) and PACIFICA (PACIFic ocean Interior CARbon) survey lines along which hydrographic datasets were obtained from 2000 to 2010. We used Ocean Data View to draw this figure [<http://odv.awi.de>].

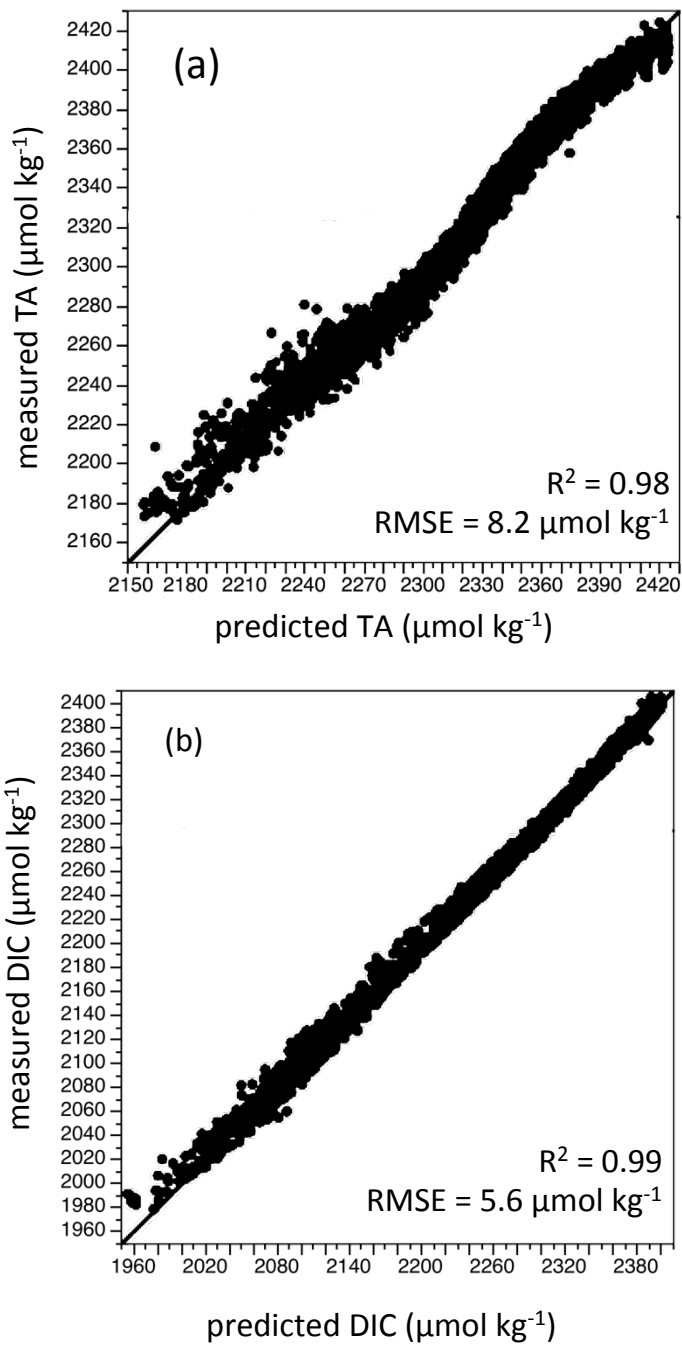


Figure 3.2

Relationships between predicted and observed values of (a) TA ($\mu\text{mol kg}^{-1}$) and (b) DIC ($\mu\text{mol kg}^{-1}$) in the subarctic North Pacific from 2000 m depth to the surface. The predicted values were obtained with Eqs. (1) and (2).

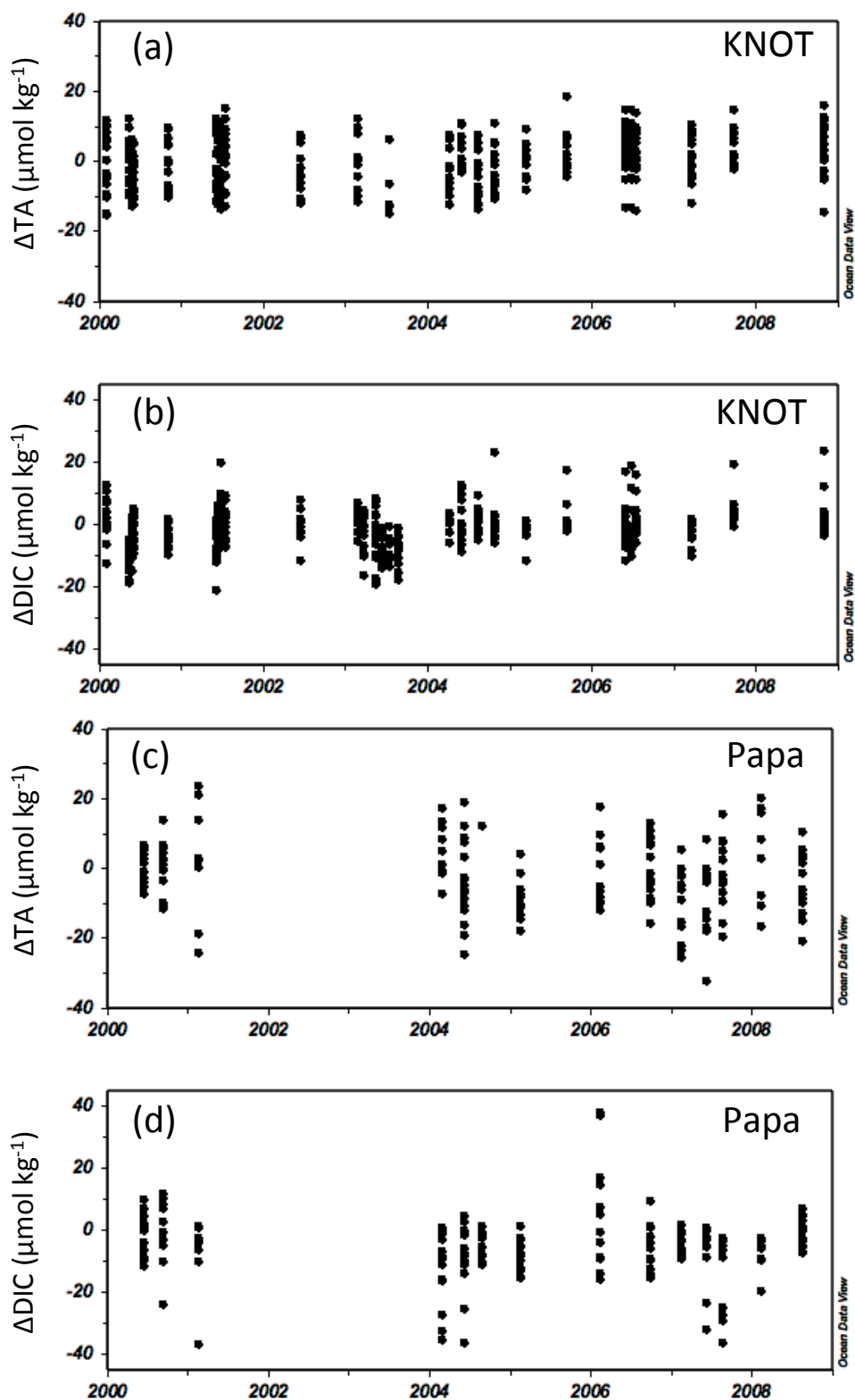


Figure 3.3

Differences between predicted and measured values of (a, c) TA ($\mu\text{mol kg}^{-1}$) and (b, d) DIC ($\mu\text{mol kg}^{-1}$) at (a, b) Station KNOT during 2001–2009 and (c, d) Station Papa during 2001–2008. A positive difference means that the predicted value is larger than the measured one. We used Ocean Data View to draw these figures [<http://odv.awi.de>].

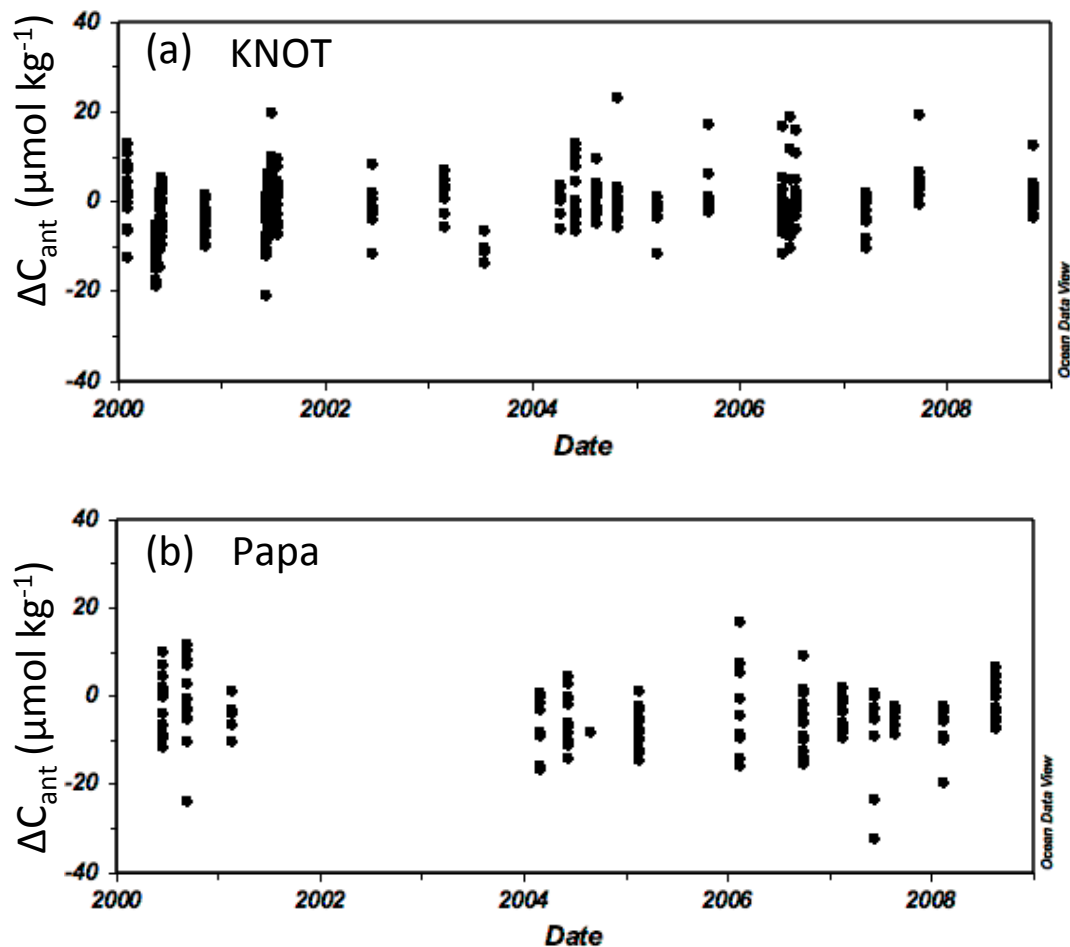


Figure 3.4

Differences in C_{ant} ($\mu\text{mol kg}^{-1}$) between values calculated from the predicted and the observed data at (a) Station KNOT during 2001–2009 and (b) Station Papa during 2001–2008. A positive difference means that the predicted value is larger than the measured one. We used Ocean Data View to draw these figures [<http://odv.awi.de>].

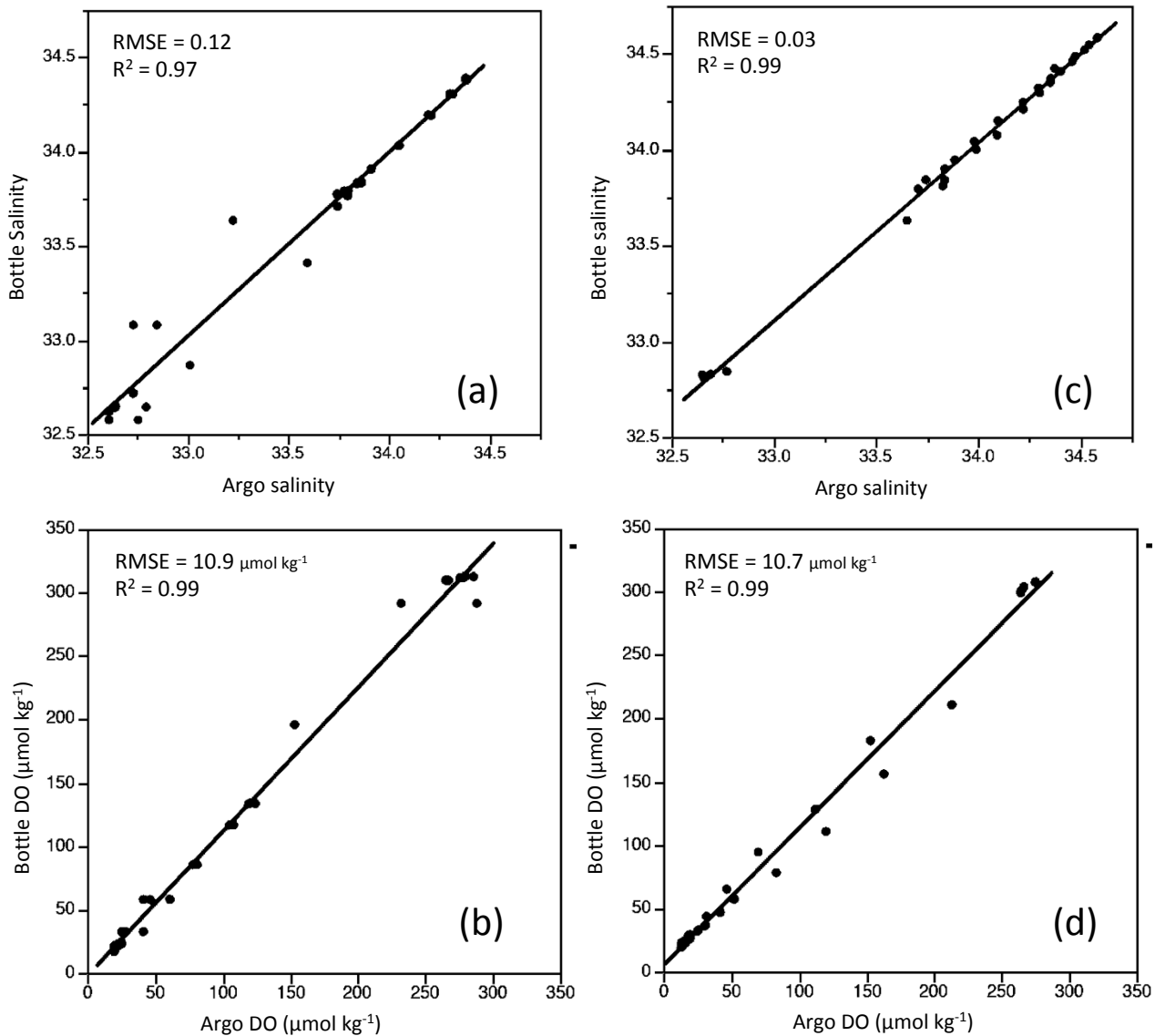


Figure 3.5

Relationships between the discrete bottle data and Argo values of S and DO ($\mu\text{mol kg}^{-1}$) in the subarctic North Pacific from 40 to 2000 m depth. (a, c) Salinity for 2900540 and 5904106, respectively. (b, d) DO for 2900540 and 5904106, respectively.

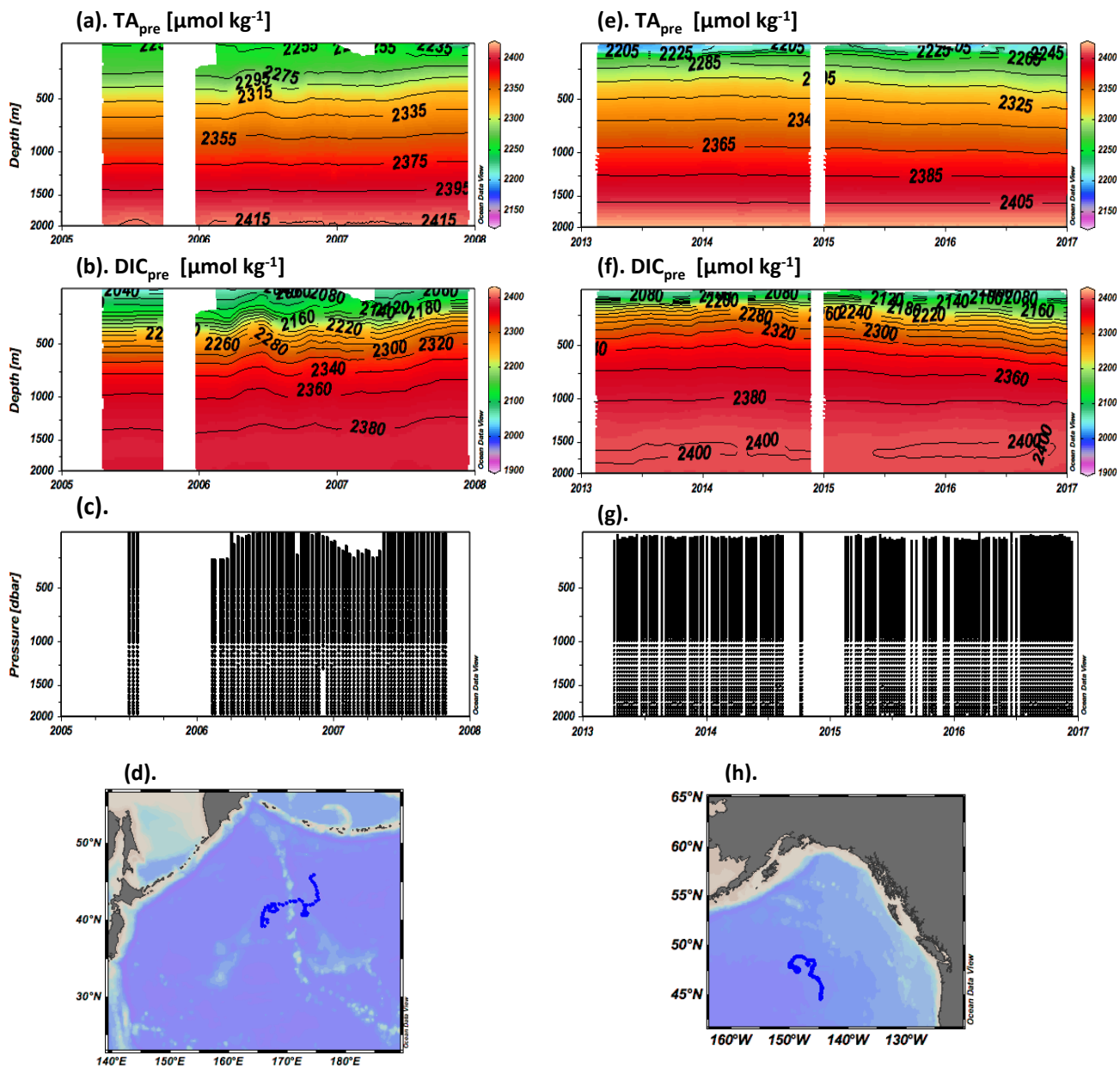


Figure 3.6

Vertical distributions of (a, e) TA_{pre} (μmol kg⁻¹) and (b, f) DIC_{pre} (μmol kg⁻¹) above 2000 m depth predicted by applying our parameterizations to DO, T and S data from Argo profiling floats 2900540 and 5904106. (c, g) Sampling profiles and (d, h) trajectory maps of Argo profiling floats 2900540 and 5904106, respectively. We used Ocean Data View to draw these figures [<http://odv.awi.de>].

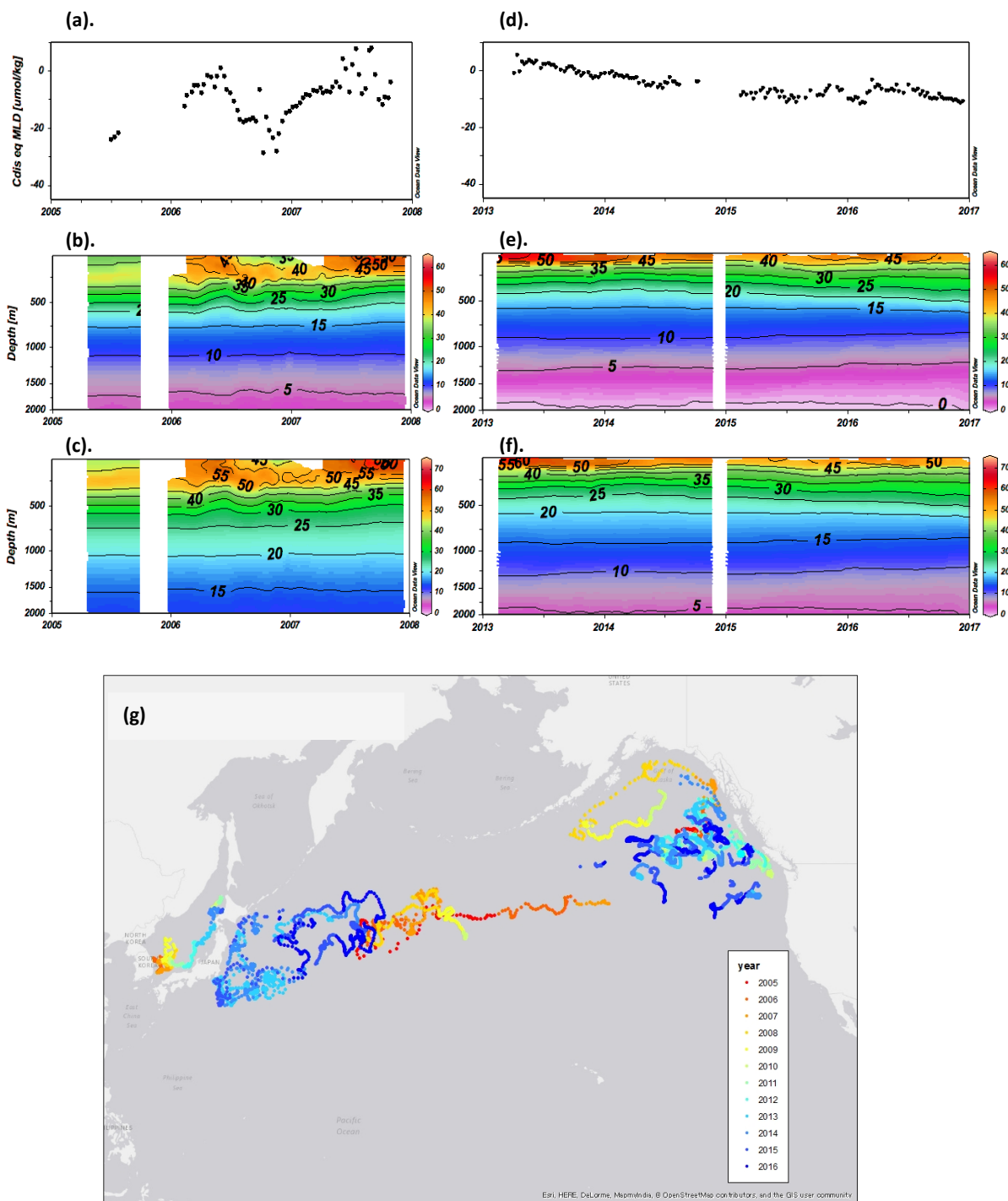


Figure 3.7

Vertical distributions of (a, d) $C_{dis\ eq\ MLD}$ ($\mu\text{mol kg}^{-1}$), (b, e) C_{res} ($\mu\text{mol kg}^{-1}$), and (c, f) C_{ant} ($\mu\text{mol kg}^{-1}$) predicted by applying our parameterizations to DO, T, and S data from the Argo profiling floats 2900540 and 5904106. The vertical axis of (b, e, c, f) has been stretched at the top part of each panel. We used Ocean Data View to draw (a)-(f) [<http://odv.awi.de>]. (g) Map of BGC Argo float trajectories in the subarctic North Pacific; the trajectories in different years are shown by the coloured dots.

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Chapter 4

Effect of vertical mixing on anthropogenic carbon variation between Okhotsk Sea and North Pacific

4.1 Introduction

There is now a great interest in understanding the global carbon cycle on the earth because of the greenhouse effect of CO₂ on the Earth's climate. Oceans absorb almost one fourth of the CO₂ released by anthropogenic activities since the industrial revolution [*Le Quere et al.*, 2014]. Marine carbon systems control both the ocean biogeochemistry cycles and the climate. As a result of burning fossil fuels, atmospheric CO₂ levels increase and the ocean carbon cycle may experience significant changes [*Feely et al.*, 2009]. As an important buffer effect on the environmental change, the ocean uptakes the CO₂ from the atmosphere and changes its chemical equilibrium, which consequently decreases the seawater pH by 0.1 units since 1750 [*Pearce et al.*, 2014]. Decreasing of surface ocean pH, in combination with rising surface temperatures, has a strong effect on the marine organisms and acts to reduce the ocean buffer capacity for CO₂ [*Doney et al.*, 2009]. Therefore, it is important to understand how and where the CO₂ system changes in the ocean.

The Okhotsk Sea (OS) is a subarctic marginal sea in the western North Pacific and the southernmost sea ice production area in the northern hemisphere. The densest water ventilating in the North Pacific region originates over the northwestern continental shelf of the OS [*Kitani*, 1973]. The North Pacific Intimide Water (NPIW) is widely distributed over the North Pacific, which influences the climate of the North Pacific. Previous studies showed that this NPIW contains a large amount of anthropogenic CO₂ (e.g., [*Sabine et al.*, 2004; *M. Wakita et al.*, 2005]). On the other hand, the capability to absorb CO₂ in the Okhotsk Sea declined due to global warming [*Watanabe et al.*, 2013].

In the Straits of the Kuril Islands area that connects OS to the North Pacific Ocean, it is reported that strong vertical mixing occurs when strong tidal currents cross the strait, and seawater

violently mixes up and down [Ohshima *et al.*, 2005]. During this strong vertical mixing, CO₂ under the surface ocean may be released into the atmosphere and may have a negative feedback for anthropogenic CO₂ uptake.

Generally, different approaches for determining the total inventory of C_{ant} in the ocean interior or the change of such C_{ant} between two successive cruises along same transect are discussed in some previous researches. For example, the ΔC* approach applied by Gruber *et al.* [1996] defined C_{ant} as follows:

$$C_{ant} = \Delta C^* - C_{diseq} \quad (4.1)$$

ΔC* can be determined by carbon chemistry equations and the biological activity can be determined by the relationship with oxygen. CO₂ at the ocean surface takes about six months to equilibrate with the atmosphere in the surface mixed layer, longer than typical mixed layer circulation timescales, such that CO₂ is out of equilibrium with the atmosphere e.g., [Gruber *et al.*, 1996]. The second term on the right hand of eq. (1), C_{diseq}, shows this disequilibrium content of CO₂. In this previous tracer age method, we assumed that the C_{ant} in the deep ocean which formed before pre-industrial period did not contain anthropogenic inorganic carbon and calculate the disequilibrium CO₂ with C_{ant} = 0 in eq. (1) and obtain the C_{diseq} using seawater age (e.g., [Sabine *et al.*, 2004]). The measurement of tracer age like CFC-12, SF₆, and C¹⁴ were complicated. If there is no trace age information we cannot calculate C_{ant} from pre-industrial. Some other methods, like Multivariate Linear Regression (MLR) and the Extended Multivariate Linear Regression (eMLR) approach (e.g., [van Heuven *et al.*, 2011; Williams *et al.*, 2015]), can allowed us to estimate the variation of C_{ant} from one period to another. These kinds of method need replicate observation of carbon species at least two times at the same area and the same depth. In the North Pacific, carbon species also changed in a 20

years cycle [Watanabe et al., submitted]. These methods cannot represent this 20 years cycle and may cancel the cycle change. In these situations, C_{ant} will be overestimated or underestimated.

Here, we tried to use a new method to estimate the C_{diseq} without trace age information. Then, we applied this method to C_{ant} estimation from the influx and runoff between the subarctic North Pacific Ocean and Okhotsk Sea, and calcify the effect of vertical mixing on carbon cycle.

3.2 Data and Methods

3.2.1 Data and sampling site

We collected the DIC and TA samples for our semi-closed method during the cruise of Multanovsky during June – July of 2014 (Mu14). Fig. 1 showed the map of all sampling stations of Mu14. We defined the three observation sections from the north to the south as line A, B and C, respectively.

Using 10-liter Niskin bottles equipped with a CTD, we drew seawater samples into a 200 ml glass bottle for DIC and TA. After opening the vent of the Niskin bottle, we prewashed the bottle three times and overflowed it by 1.5 times as its volume. As recommended by Dickson et al. (2007), we poisoned the sample by 100 μ L saturated HgCl_2 solution to prevent biological activity from altering the carbon amount in the sample vessel before analysis. Using a 200 mL vessel to collect seawater samples, we left a headspace of about 3 mL to avoid the breakage of the glass vessel because of the expansion of the seawater sample upon warming. The sampling bottles are stored during the cruise at a room temperature and the content of DIC and TA were measured by semi-closed cell method. In this study, we used the results of southern observational sites of the cruise to discuss the relationship between measured carbon species and other general hydrographic data (e.g. temperature (T), Salinity (S)). We collected two sets of duplicate samples at each station (both in shallow and deep layers). The precisions of analysis for replicate water samples were usually less than 1.8 $\mu\text{mol/kg}$ for DIC and 1.2 $\mu\text{mol/kg}$ for TA. The accuracy and precision of Certified Referenced Materials (CRM, provided by KANSO Co., Ltd) were 3.6 $\mu\text{mol/kg}$ and 1.7 $\mu\text{mol/kg}$ for DIC, 0.7 $\mu\text{mol/kg}$ and 1.3 $\mu\text{mol/kg}$ for TA. We also compared the DIC and TA at a depth of 2,500 m measured by our semi-closed cell method with the previously observed DIC and TA data at same observational sites by *Watanabe and Wakita* (2004) which is published in the PACIFIC ocean Interior CARbon (PACIFICA) data set [*Suzuki et al.*, 2013]. Based on the data of DIC and TA collected in this study, we calculated pH and the saturation of

aragonite (Ω_{AR}) using thermodynamic equations of the seawater carbon chemistry [Dickson *et al.*, 2007]. In all of these calculations, we used the seawater pH scale.

3.2.2 Estimations of disequilibrium DIC (C_{diseq}) and anthropogenic DIC (C_{ant})

CO_2 at the ocean surface takes about six months to equilibrate with the atmosphere in a 40-meter mixed layer [Sarmiento and Gruber, 2006], longer than typical mixed layer circulation timescales, such that CO_2 is out of equilibrium with the atmosphere. The degree of disequilibrium depends on both the circulation timescale and on the biological time-scale (at which biology incorporates carbon into organic matter). Here we depended on a new assumption about this disequilibrium DIC (C_{diseq}) value without tracer age information discussed in other previous studies and estimated C_{ant} using the same method as described in chapter 3 with observed DIC and TA instead of predicted DIC and TA,

According to the concepts outlined in Gruber and Sarmiento (2006), anthropogenic DIC (C_{ant}) can be written as

$$C_{ant} = DIC - C_{pi, sat} - C_{soft} - C_{carb} - C_{diseq} \quad (4.2)$$

where $C_{pi, sat}$ (preindustrial saturated DIC), C_{ant} and C_{diseq} are preformed components and C_{soft} , which is derived from the remineralization of organic matter, and C_{carb} , which is derived from the dissolution of $CaCO_3$ (see below), are regenerated components. Here, we used the measured DIC collected from cruise Mu14.

$C_{pi, sat}$ can be calculated from the equilibrium carbon chemistry relationships as follows:

$$C_{pi, sat} = f(TA_0, pCO_2 = 280 \text{ ppm}, T, S, P) \quad (4.3)$$

where TA_0 is preformed TA from the surface ocean obtained from the linear relationship between TA_0 and S ($TA_0 = 399 + 54.629S$)⁵. We calculated the contribution of remineralization of organic matter to DIC as

$$C_{\text{soft}} = 117/170 \text{ AOU} \quad (4.4)$$

where 117/170 is the Redfield ratio of carbon to oxygen⁶ and AOU is apparent oxygen utilization. AOU is calculated as the difference between saturated DO and observed DO. Here, we assumed that the Redfield ratio of carbon to oxygen was constant vertically and used the N : C : O₂ ratio of 16 : 117 : (− 170) [Anderson and Sarmiento, 1994]. We calculated the contribution from the dissolution of CaCO₃ as follows:

$$C_{\text{carb}} = 0.5(TA - TA_0 - 16/170 \text{ AOU}) \quad (4.5)$$

where 16:170 is the Redfield ratio of nitrogen to oxygen [Anderson and Sarmiento, 1994]. The term 16/170AOU corrects the calculation for the fact that TA also includes nitrate formed by the remineralization of organic matter. The coefficient 0.5 indicates that a change of one mole in TA corresponds to a change of one-half mole in DIC. Here, we used the measured TA collected from cruise Mu14.

We also did not use the traditional method to calculate the disequilibrium DIC in seawater Gruber *et al.* (1996), because we did not have any seawater age information. Therefore, assuming that the CO₂ disequilibrium value would be constant from the surface mixed layer to the ocean interior, we estimated the CO₂ disequilibrium value at the mixed layer depth (MLD) ($C_{\text{diseq, MLD}}$) by subtracting the preformed and regenerated components at the MLD (saturated DIC at MLD ($C_{\text{sat, MLD}}$) and C_{soft} and

C_{carb} at MLD ($C_{\text{carb,MLD}}$ and $C_{\text{carb,MLD}}$), respectively) from DIC_{pre} at the MLD ($\text{DIC}_{\text{pre MLD}}$). $C_{\text{diseq,MLD}}$ was calculated as follows:

$$C_{\text{sat,MLD}} = f(\text{TA}_0, \text{pCO}_2 = 395 \text{ ppm}, T, S, P) \quad (4.5)$$

$$C_{\text{diseq,MLD}} = \text{DIC}_{\text{pre,MLD}} - C_{\text{sat,MLD}} - C_{\text{soft,MLD}} - C_{\text{carb,MLD}} \quad (4.6)$$

We here used the pCO_2 value of 395 ppm in Eq. (4.5).

4.3. Results and Discussion

4.3.1 Vertical distributions of carbon species

We showed the vertical distribution of Ω_{AR} along isopycnal surface in Fig. 4.2. Seawater in the upper layers was supersaturated ($\Omega_{AR} > 1$) along three observation sections and decreased with increased depth. At line A, saturation horizon ($\Omega_{AR} = 1$ contour) in the west (the Okhotsk Sea part) was at about 50 m deeper than in the east (the Pacific part). Additionally, the saturation horizon was at about 125 m in the east of line A in the exit of Okhotsk Sea and about 5 – 10 m deeper than at line B and C in north. These distributions also showed the evidence that vertical mixing can change the ocean carbon species distribution and have a buffering effect on ocean acidification.

As showed in Fig. 4.3, pH in Okhotsk Sea was 0.18 higher than in the North Pacific. This increase in pH could be explained by the increase in alkalinity in the Amur River, in previous study, they suggest that the high TA seawater from the Okhotsk Sea could mitigate one-fifth of recent ocean acidification in the North Pacific [Watanabe *et al.*, 2009]. We calculated the differences of $pH_{25^\circ C}$ and $pH_{in situ}$ ($\Delta pH_{25^\circ C}$ (pH calculated in $25^\circ C$) and $\Delta pH_{in situ}$ (pH in in-situ temperature)) between line C and B, line B and A, at different isopycnal surfaces ($\sigma_\theta = 26.7, 26.8, 26.9, 27.0$) in the North Pacific Part (Table 1). From line B to line C, absolute ΔpH values from $\sigma_\theta = 26.7$ surface to 27.0 surface decreased gradually. This high pH seawater mixed with the surrounding Pacific part of line A higher pH was observed than other lines.

Through a strong vertical mixing, the subsurface water may communicate with the atmosphere and the high concentration of CO_2 absorbed in the Okhotsk Sea may be released to the atmosphere. In order to clarify this assumption, we calculated the C_{ant} in this region in the following sections.

4.3.2 C_{diseq} in Okhotsk Sea and North Pacific

As introduced before, here, we had no data to determine the seawater age, so we could not use the traditional method of estimating C_{diseq} due to disequilibrium in the air–sea exchange. CO_2 absorbed from the atmosphere enter the ocean interior from the isopycnal surfaces. We assumed that the CO_2 in the surface mixed layer can communicate with the atmosphere very well and the CO_2 concentration at the bottom of surface mixed layer was the value that just before it enter the subsurface. We used the disequilibrium CO_2 at this surface mixed layer bottom as the C_{diseq} under surface mixed layer and also assumed it will be constant vertically.

Before the calculation of C_{ant} , we compared the C_{diseq} of each line with previous studies to confirm if C_{diseq} calculated by our new method are in a general ranges. The average disequilibrium values in line A, line B and line C were $-18.2 \pm 8 \mu\text{mol kg}^{-1}$, $-15.4 \pm 9 \mu\text{mol kg}^{-1}$ and $-14.3 \pm 4 \mu\text{mol kg}^{-1}$, respectively, which were consist with the results of *Gruber et al.* [1996] in the North Atlantic ($-13 \pm 4 \mu\text{mol kg}^{-1}$) (Fig. 4.4). This is good evidence for that our assumption is also effectual for evaluating the C_{ant} using not only Argo and other higher-solution ocean hydrographic data but also observed data. However, based on the assumption of this study, this method cannot calculate the C_{diseq} in the surface mixed layer accurately. We applied the average values of C_{diseq} in line A, B, C to calculate C_{ant} in these three lines under surface mixed layers.

4.3.3 Comparison of C_{ant} in the entrance and exit of Okhotsk Sea

Assuming that C_{diseq} in the line B (entrance) and line A (exit) of Okhotsk Sea are constant vertically as the average value of -18.2 と $-15.4 \mu\text{mol/kg}$, respectively, we obtained the vertical distributions of C_{ant} in each lines in Fig.3. The maxima of C_{ant} are in the upper 300 m layers (Fig. 4.5).

In the line B where seawater entrances the Okhotsk Sea, C_{ant} penetration depth was almost at the $26.9\sigma_\theta$ depth. Before exiting the Okhotsk Sea, in the western part of line A, C_{ant} was as deep as $27.2\sigma_\theta$. This is corresponding to previous studies that the total influx of anthropogenic carbon

in the Okhotsk Sea was $10 \text{ gC m}^{-2} \text{ yr}^{-1}$, which is twice larger than that in the global ocean ($5.0 \text{ gC m}^{-2} \text{ yr}^{-1}$) [Masahide Wakita *et al.*, 2003]. In the strait area of line A, penetration depth of C_{ant} became shallower sharply. It showed the possibility that the C_{ant} absorbed in the Okhotsk Sea has been released to the atmosphere by the strong vertical mixing. This result showed a evidence that the strait connecting Okhotsk Sea and North Pacific has a buffering effect on the absorption of the C_{ant} .

4.4 Concluding remarks

In the boundary area between the North Pacific subarctic region and the Okhotsk Sea, we used a new method to estimate the C_{diseq} without trace age information and applied this C_{diseq} to C_{ant} estimation from the influx and runoff between the subarctic North Pacific Ocean and Okhotsk Sea, and calcify the effect of vertical mixing on carbon cycle. The efficiency in oceanic absorption of anthropogenic carbon in the Okhotsk Sea has already decreased by 10-16 % from 1980s to 2000s [Watanabe *et al.*, 2013; Watanabe *et al.*, 2001]. Previous study showed that the recent reinforcement of ocean stratification derived from the ocean warming caused the weakening of water ventilation in the Okhotsk Sea, and the penetration of atmospheric anthropogenic carbon to the deep ocean interior is becoming difficult [Watanabe *et al.*, 2013]. Additionally, in this study, we showed that the anthropogenic components of CO_2 might be released by the strong vertical mixing. Using this method, we can only calculate the C_{ant} under surface mixed layer.

Table

Table 4.1 Differences of pH in each isopycnal layers (26.7 – 27.0)

	σ_{θ}	$\Delta\text{pH}_{25^{\circ}\text{C}}$	$\Delta\text{pH}_{\text{in situ T}}$
Line C → line B	26.7	-0.176 ± 0.056	-0.013 ± 0.101
	26.8	-0.284 ± 0.009	-0.035 ± 0.036
	26.9	-0.223 ± 0.036	0.004 ± 0.041
	27.0	-0.288 ± 0.022	0.022 ± 0.035
Line B → line A	26.7	0.044 ± 0.023	0.038 ± 0.111
	26.8	0.046 ± 0.027	0.057 ± 0.040
	26.9	0.028 ± 0.023	0.096 ± 0.043
	27.0	0.020 ± 0.009	0.026 ± 0.037

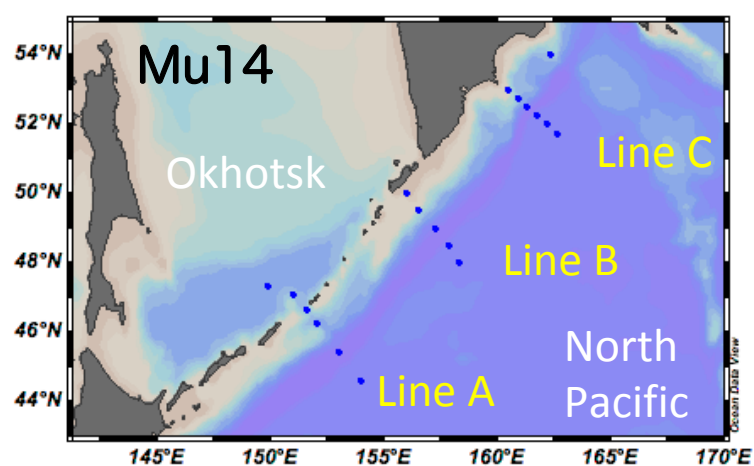


Figure 4.1

Sampling site for DIC and TA during the cruise of Multanovsky during June – July of 2014 (Mu14). We used Ocean Data View to draw this figure [<http://odv.awi.de>]. We defined the three observation lines from the south to north as line A, line B and line C, respectively.

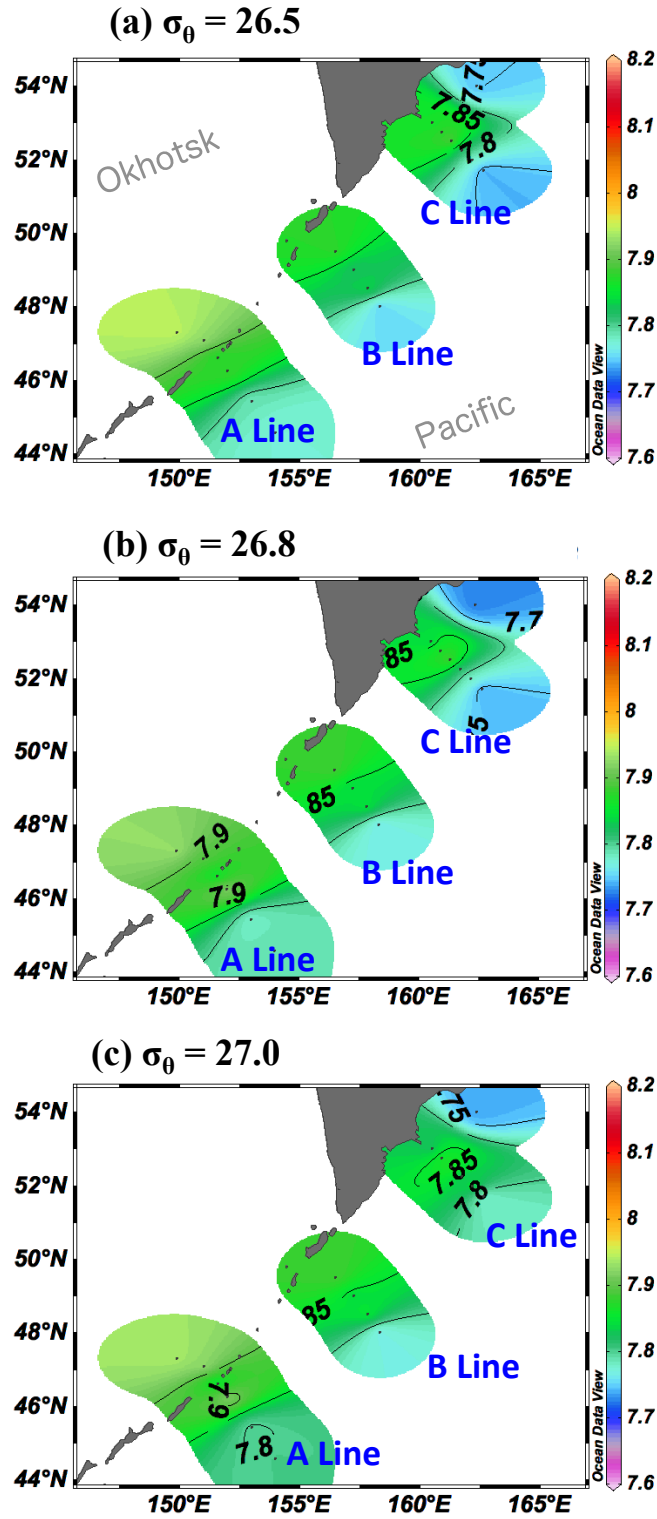


Figure 4.2

Distributions of $\text{pH}_{25^\circ\text{C}}$ of (a) $\sigma_\theta = 26.5$, (b) $\sigma_\theta = 26.5$, (c) $\sigma_\theta = 26.5$ isopycnal surfaces. We used Ocean Data View to draw (a)-(f) [<http://odv.awi.de>].

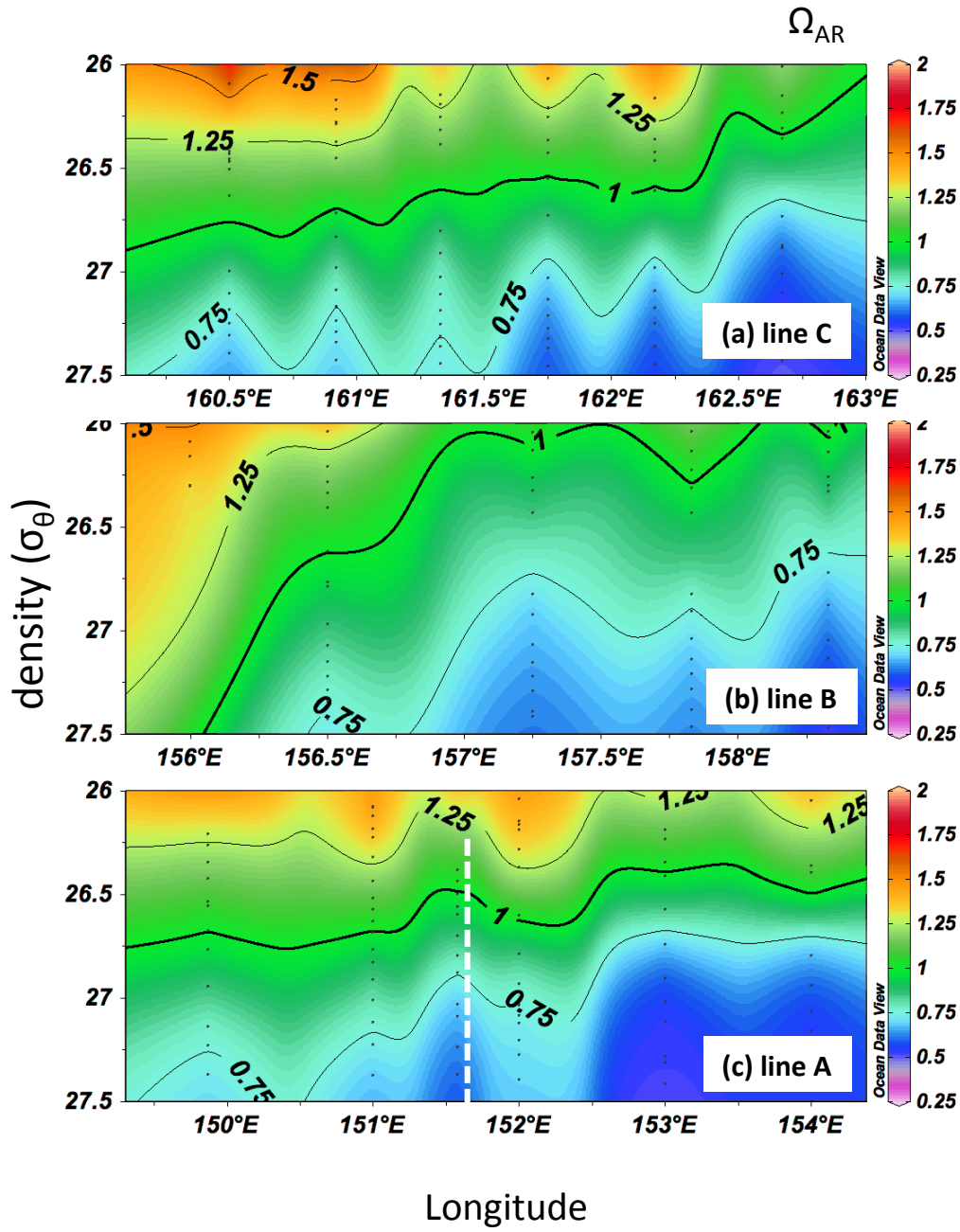


Figure 4.3

Vertical distributions of Ω_{AR} ($\mu\text{mol kg}^{-1}$) in (a) line C, (b) line B, (c) line A of cruise Mu14. We used Ocean Data View to draw (a)-(f) [<http://odv.awi.de>].

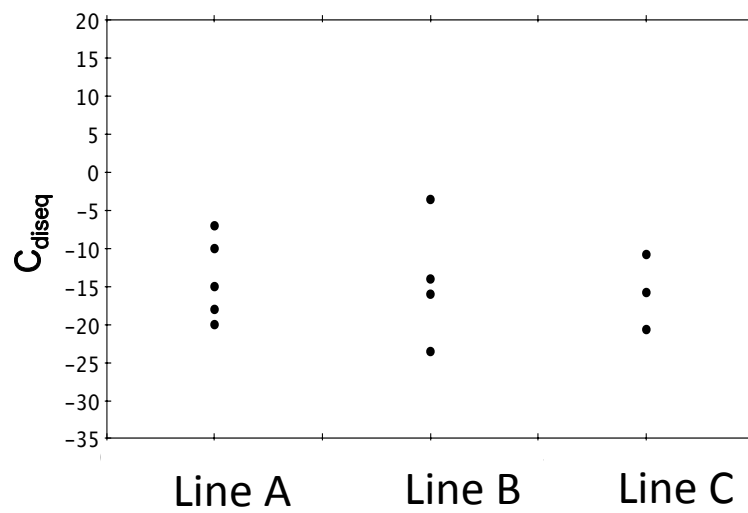


Figure 4.4

C_{diseq} ($\mu\text{mol kg}^{-1}$) in line A, line B, and line C of cruise Mu14.

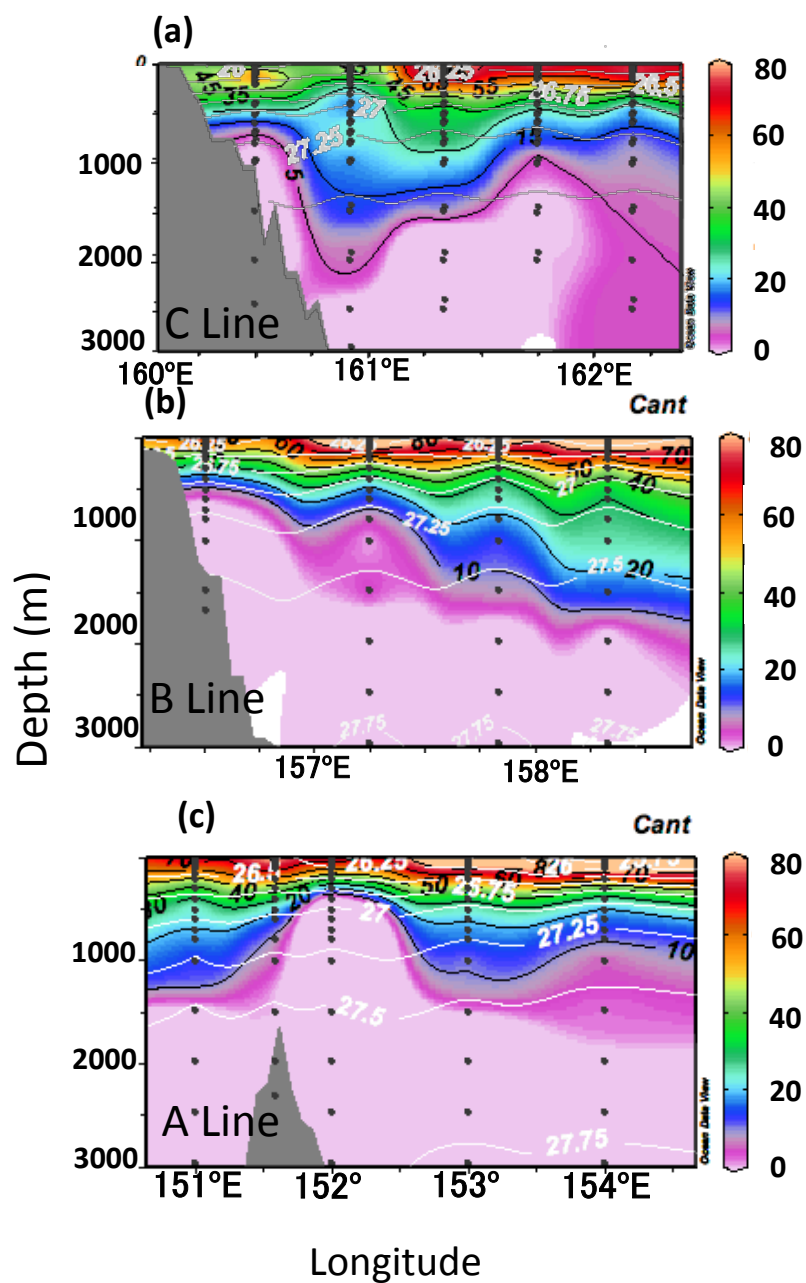


Figure 4.5

Vertical distributions of C_{ant} ($\mu\text{mol kg}^{-1}$) estimated from (a) line C, (b) line B, (c) line A of cruise Mu14. We used Ocean Data View to draw (a)-(f) [<http://odv.awi.de>].

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Chapter 5

General conclusion

The ocean's uptake of anthropogenic CO₂ has been causing global ocean acidification. In this research, we attended to obtain a high-resolution spatiotemporal distribution of oceanic carbon chemistry and also estimate anthropogenic CO₂ in a new method without seawater age information,

In Chapter 1, we provided parameterizations to speculate changes in the vertical distributions of the seawater total alkalinity (TA), dissolved inorganic carbon (DIC), and pH by using all available observations of dissolved oxygen (DO, $\mu\text{mol kg}^{-1}$), water temperature (T, $^{\circ}\text{C}$), and salinity (S) data from previous high quality datasets of ocean hydrographic properties. All datasets were collected in the North Pacific subpolar region during the period of 2000 to 2010, for 40–400 m depth, and between 40°N–56°N, 145°E–130°W). Root mean square errors for the parameterizations with 7.4 $\mu\text{mol kg}^{-1}$ for TA, 7.1 $\mu\text{mol kg}^{-1}$ for DIC, and 0.02 for pH were obtained with R^2 of more than 0.95. To evaluate the validity of these parameterizations, we compared measured TA, DIC, and pH with predicted values. The differences were almost within 10 $\mu\text{mol kg}^{-1}$ for TA and DIC, and 0.05 for pH. Applying our parameterizations to the climatological datasets of DO, T, and S data from World Ocean Atlas 2009, we reconstructed seasonal and monthly vertical distributions of seawater TA, DIC, and pH. Furthermore, by substituting our parameterizations into detailed vertical distributions of DO, T, and S data measured bi-weekly by automatic ocean hydrographic sensors from Argo profiling floats, we described the detailed vertical spatiotemporal distributions of seawater TA, DIC, and pH. In the North Pacific subpolar region, in the case that there is no time-series of ocean carbon species, our parameterizations allowed us to elucidate the dynamics of ocean carbon chemistry from two-week scale to decadal scale.

In Chapter 2, considering the penetration depth of anthropogenic CO_2 , we developed new parameterizations of the TA, DIC and pH from the ocean's surface to 2000 m depth by using DO, T, S, and P data over the same area as Chapter 1. We then used the values of TA and DIC predicted by DO, T, S, and P data collected by autonomous profiling floats with biogeochemical sensors delivering those data in quasi-real-time, and we described the distribution of oceanic anthropogenic CO_2 in the 2000s in the subarctic North Pacific at high spatiotemporal resolution and with a precision of $\pm 6.9 \mu\text{mol kg}^{-1}$. They can also reconstruct oceanic carbon chemistry within decadal scale. Disequilibrium DIC (C_{diseq}) in seawater is an important factor to clarify C_{ant} and a useful indicator to estimate gas exchange of various gases at the air-sea interface. Traditional methods to calculate C_{diseq} need the age information of water mass predicted by chemical tracers in discrete collected deep water samples, so that it is hard to obtain C_{diseq} in detailed spatial distribution on ocean basin scale. We developed a new method to estimate the C_{diseq} without the information of water mass age, and consequently this method allowed us to obtain C_{diseq} that was consistent with the traditional method. This new method for estimating C_{diseq} can be broadly applied to Argo or other high-resolution ocean hydrographic data set in the future. Using the parameterized TA and DIC values, we found anthropogenic CO_2 in this region at 1900 m depth, about 300 m deeper than its maximum depth during the 1990s, and its average inventory to 2000 m was $24.8 \pm 10.2 \text{ mol m}^{-2}$, about 20% higher than the average during the 1990s. Future application of our parameterization method to BGC Argo data from the global ocean should make it possible to map the detailed spatiotemporal distribution of CO_2 cycle parameters at high resolution in the global ocean.

In Chapter 3, we used this new method to estimate the C_{diseq} without trace age information and applied this C_{diseq} to C_{ant} estimation from the influx and runoff between the subarctic North Pacific

Ocean and Okhotsk Sea, and calcify the effect of vertical mixing on carbon cycle. We showed that the anthropogenic components of CO_2 might be released by the strong vertical mixing in this region.

In the future, we will compare our new method to estimate C_{diseq} to the traditional method. In order to estimate the anthropogenic CO_2 more precisely, we will also apply this new method to estimate C_{diseq} to more Argo data set and obtain the seasonal and local variations of C_{diseq} . In this study, we just tested the parameterization technics in the subarctic Pacific Ocean. We attended to extent this technics to the whole world ocean, and map the high-resolution map of ocean carbon chemistry in a world ocean scale. In this study, we almost show the lagrangian variation of DIC, TA, and pH when we used the Argo data. In the future, we will also collect Argos moved in a specific region and connect the different Argo data in a time scale together as a time-series data. Applying these data to our parameterizations, we can make a monitor system to observe long trend change of the ocean carbon chemistry like time-series stations (e.g., ALOHA, KNOT).

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