

Reconstruction of pH in the Surface Seawater over the North Pacific Basin for All Seasons Using Temperature and Chlorophyll-*a*

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(Received 13 April 2004; in revised form 8 September 2004; accepted 14 September 2004)

We found a simple function of pH that relates to sea surface temperature (SST, K) and chlorophyll-*a* (Chl, $\mu\text{g l}^{-1}$) using measured surface seawater pH, SST and Chl data sets over the North Pacific: $\text{pH} (\text{total hydrogen scale at } 25^\circ\text{C}) = 0.01325 \text{ SST} - 0.0253 \text{ Chl} + 4.150$ ($R^2 = 0.95$, $p < 0.0001$, $n = 483$). Moreover, evaluating the seasonal variation of pH based on this algorithm, we compared the measured pH with the predicted pH at the observational time series stations in subpolar and subtropical regions. The average of ΔpH (measured – predicted, $n = 52$) was 0.006 ± 0.022 pH. Therefore, the combination of SST and Chl can allow us to determine the spatiotemporal distribution of pH over the North Pacific. Using the climatological data sets of SST and Chl with our pH algorithms, we have described the seasonal distributions of pH at 25°C ($\text{pH}_{(25)}$) and pH *in situ* temperature ($\text{pH}_{(T)}$) over the North Pacific surface water.

Keywords:

- Reconstruction of pH,
- sea surface temperature,
- chlorophyll-*a*,
- North Pacific basin.

1. Introduction

To observe the spatiotemporal variations in oceanic carbonate systems, many agencies have carried out surveys over the world oceans during the 1990s. However, most of these observations provide only snapshot data, which might be insufficient to describe the spatiotemporal changes of the oceanic carbonate system on the ocean basin scale.

Several studies have attempted to parameterize CO_2 fugacity ($f\text{CO}_2$), dissolved inorganic carbon (DIC) and total alkalinity (TA) using sea surface temperature (SST), nutrients and salinity (Stephens *et al.*, 1995; Wanninkhof *et al.*, 1996; Millero *et al.*, 1998; Boutin *et al.*, 1999; Lee *et al.*, 2000; Loukos *et al.*, 2000). However, these algorithms are limited to seasons and/or local oceanic regions only. In the study of climate change, it is necessary to cover data sets at least at basin and decadal scale with various oceanic conditions. If the above algorithms are applied over the basin scale, a large estimation error will occur. Therefore, it is desirable that carbonate species can be expressed by only one algorithm that holds through all seasons and on a basin-wide scale.

However, since relatively few high-precision pH data have been obtained as yet, the use of pH and other pa-

rameters have resulted in few algorithms for the surface water pH, and these are limited to local regions (Poisson and Chen, 1987; Terner *et al.*, 2001). The measurement of pH with high precision has been improved recently (e.g. Ono *et al.*, 1998). Thus, we here try to parameterize pH using these recent pH data over the North Pacific at a large, basin-wide scale.

Seawater pH is a key variable underlying many physical and biological processes in the ocean. It is essential to measure it accurately and precisely in order to characterize the marine carbonate system and biological activity quantitatively. Spectrophotometric procedures have recently been developed for measuring seawater pH with a precision up to 0.0005 pH in the laboratory (e.g. Clayton and Byrne, 1993; Zhang and Byrne, 1996). Consequently, spectrophotometric pH measurements can be obtained with a precision of 0.001 pH in the ocean. At this level of precision and sensitivity, pH measurements are useful to calculate other CO_2 parameters (DIC, TA, $f\text{CO}_2$) and as a tool in quality control assessments of other CO_2 system parameters (Clayton *et al.*, 1995; Byrne *et al.*, 1999).

The decrease of pH in seawater would be expected due to the uptake of anthropogenic CO_2 . The significant acidification of the seawater will cause major shifts in the speciation of the CO_2 system, i.e., an increase in CO_2 (aq) causes a decrease in carbonate ion (CO_3^{2-}). This shift would reduce the production of calcium carbonate min-

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eral phases such as calcite and aragonite. Such expected changes could affect marine organisms and metabolism in various ways, possibly leading to changes in biogeochemical cycles, ecosystems, and their interactions (Riebesell *et al.*, 2000). Therefore, pH is potentially a key parameter in characterizing the chemical and biological processes controlling CO₂ in the ocean.

The change of pH in seawater is mainly controlled by the factors that govern temperature and biological activity (e.g. Hunter, 1998). If one considers Chl as a potential index of biological activity, it is possible to parameterize the pH using SST and Chl. We here attempt to parameterize the pH with SST and Chl over the North Pacific for all seasons.

2. Data and Method

We observed the pH, SST and Chl in the WOCE-P1r cruise in 1999, KH-99-1 cruise in 1999 and KH-00-3 cruise in 2000 (Preliminary Report of the R/V Hakuho Maru Cruise KH-99-1, 1999; Preliminary Report of the R/V Hakuho Maru Cruise KH-00-3, 2000; Carbon Dioxide Information Analysis Center, 2003) (Fig. 1). The seawater samples were collected at depths of 0 m–30 m using a bucket (surface seawater only) and the Niskin bottle multiple sampling system with a CTD. All pH samples were stored below 5°C and analyzed promptly or at most within 12 hours after sampling using the spectrophotometric continuous flow method at 25 ± 0.03°C (Preliminary Report of the R/V Hakuho Maru Cruise KH-00-3, 2000). In this method, we used *m*-cresol purple as an indicator of pH with a 50 mm flow cell length (Clayton and Byrne, 1993). The Chl content was measured by the fluorometrical method (Holm-Hansen and Riemann, 1978). During cruise KH-99-1 (140°E line), we had no data on the Chl, so we used the Chl data obtained in the Ryofu maru cruise which was carried out within 1 month of the KH-99-1 cruise observations at the same latitude along the 137°E line (Data Report of Oceanographic Observation, 2000).

Moreover, to parameterize pH over the North Pacific, we also used the following hydrographic data obtained from three cruises and two observational time series stations (Fig. 1): NOPACCS (1996), WEST-COSMIC (1997–2001), WOCE-P2 (1993–1994), HOT (1992–2001) and KNOT (1998–2002). The sampling and analytical methods adopted during these cruises for each observed property can be found in the manual posted on each respective web site (WOCE Hydrographic Program Office, 2002; Hawaii Ocean Time-series Data Organization & Graphical System, 2003; Kansai Environmental Engineering Center, 2003; Kyodo Western North Pacific Ocean Time Series, 2003). We used the data between 0 m and 30 m since no surface data were reported on some cruises.

It is necessary to check the pH data obtained from

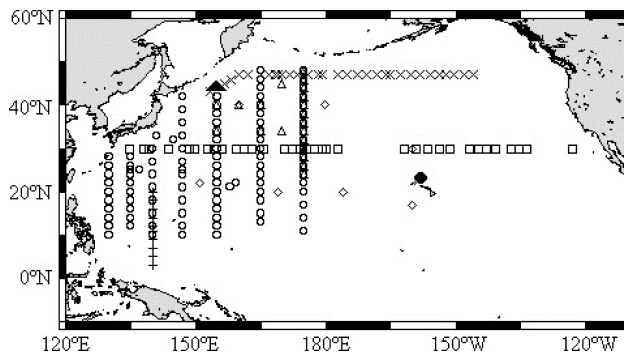


Fig. 1. Map of sampling points in the North Pacific. Time series stations HOT (22.7°N, 158°W) and KNOT (44°N, 155°E) are shown as a filled circle and a filled triangle, respectively. Each symbol represents the following cruises; open squares: WOCE-P2, open triangles: NOPACCS, open circles: WEST-COSMIC, crosses: KH99-1, X-marks: WOCE-P1r and open diamonds: KH00-3, respectively.

different cruises to ensure their mutual consistency before the algorithms are derived. All the pH data were measured by either the total hydrogen scale or the seawater scale, although these were measured at 25°C. Our pH scale was the total hydrogen scale, which is useful to calculate the oceanic carbonate system and this scale has been well used in recent years (Table 1). We therefore adjusted all the pH data measured on the seawater scale to the total hydrogen scale according to DOE, 1994 (NOPACCS, WEST-COSMIC and HOT). We also termed the measured pH at 25°C (total hydrogen scale) as $pH_{m(25)}$.

We compared these data sets of $pH_{m(25)}$ in the deep water (>3000 m) in sampling observational points where each cruise track crossed or lay within a 1° grid, assuming that the pH in the deep water does not change on a timescale of several years. In the case of HOT (22.7°N, 158°W), we compared HOT with the observational point in KH-00-3 cruise (17°N, 160°W) as this was the nearest sampling point to HOT. Moreover, to correct the difference between two different cruises, we adjusted bottle data of one cruise to that of another cruise by using the linear interpolation method to correct for the difference in depth between the two cruises. After the depth correction, we compared the salinity at the same depth to confirm the change of deep water. We found all salinity differences lay within 0.01. Therefore, we used all data sets in the deep water (> 3000 m) to estimate difference of $pH_{m(25)}$ (Kansai Environmental Engineering Center, 2003).

We used the $pH_{m(25)}$ data set of WOCE-P1r as a criterion, this data set is the most accurate because we measured pH using the spectrophotometric technique. The

Table 1. Difference in surface $\text{pH}_{\text{m}(25)}$ between the WOCE-P1r cruise and other cruises. SWS and TS represent the seawater scale and the total hydrogen scale for pH, respectively. We here show the difference of pH as pH of any cruise minus pH in the WOCE-P1r.

Cruise/Station name	Observation year	Description	Number of data (0 m–30 m)	Method	$\text{pH}_{\text{m}(25)}$ difference
HOT	1992–1997	22.7°N, 158°W	79	Spectrophotometry (SWS)	–0.008
WOCE-P2	1993–1994	30°N, 135°E–121.2°W	33	Potentiometry (TS)	–0.013
NOPACCS	1996	24°N–48°N, 155°E–175°W	70	Potentiometry (SWS)	0.055
WEST-COSMIC	1997–2001	10°N–48°N, 130°E–175°W	172	Potentiometry (SWS)	0.055
KNOT	1998–2002	44°N, 155°E	53	Potentiometry (TS)	0.024
KH99-1	1999	3°N–20°N, 140°E	7	Spectrophotometry (TS)	0.012
WOCE-P1r	1999	43.2°N–47°N, 153.3°E–145.8°W	48	Spectrophotometry (TS)	—
KH00-3	2000	17°N–40°N, 151°E–160°W	14	Spectrophotometry (TS)	0.006

accuracy of pH was verified by the DIC and TA that were certified using reference material distributed by A. G. Dickson of the Scripps Institution of Oceanography (SIO-CRM). It was not possible to compare directly the $\text{pH}_{\text{m}(25)}$ on the cruises of WOCE-P2, KH99-1, KH00-3 and HOT due to the lack of crossing points with the WOCE-P1r cruise route. We here compared the $\text{pH}_{\text{m}(25)}$ between these cruises and the other cruise (WEST-COSMIC) having crossing points with the WOCE-P1r cruise. The averaged differences are shown in Table 1. We corrected the values of pH by deducting these differences from $\text{pH}_{\text{m}(25)}$ of each cruise. We also used the Chl data without any correction of the offsets since the Chl data are limited to the upper layer.

The differences in $\text{pH}_{\text{m}(25)}$ between WOCE-P1r (47°N, 174°E) and NOPACCS (46°N, 175°E) and WEST-COSMIC (46°N, 175°E) were 0.055 pH, which is greater than the differences of $\text{pH}_{\text{m}(25)}$ with the other cruises (Table 1). These differences may be caused by the characteristics of both the pH scale and the analytical method. However, the same laboratories analyzed the NOPACCS and WEST-COSMIC data sets. Moreover, the difference in $\text{pH}_{\text{m}(25)}$ between the NOPACCS and WEST-COSMIC was 0.0004 pH. We corrected the offset of 0.055 pH for the NOPACCS and WEST-COSMIC data sets.

3. Results and Discussion

3.1 Parameterization of $\text{pH}_{\text{m}(25)}$ in the surface seawater over the North Pacific using SST and Chl

Using the corrected $\text{pH}_{\text{m}(25)}$ data sets in Table 1, we

attempted to relate the surface $\text{pH}_{\text{m}(25)}$ with SST (K) and Chl ($\mu\text{g l}^{-1}$) over the North Pacific. We used the $\text{pH}_{\text{m}(25)}$ to parameterize pH because the relative error of $\text{pH}_{\text{m}(25)}$ was smaller than that of pH under the *in situ* seawater temperature (pH_{T}). Using a simple two-parameter function of $\text{pH}_{\text{m}(25)}$ with SST and Chl, the predicted pH ($\text{pH}_{\text{p}(25)}$) was given as

$$\text{pH}_{\text{p}(25)} = 0.01325 \text{ SST} - 0.0253 \text{ Chl} + 4.150$$

(RMSE = 0.025, $R^2 = 0.95$, $p < 0.0001$, $n = 483$). (1)

In Eq. (1), $\text{pH}_{\text{p}(25)}$ has a strong correlation with SST ($t = 57.52$, $p < 0.001$) and Chl ($t = -4.77$, $p < 0.001$) (Fig. 2). The effects of measurement errors of SST and Chl on $\text{pH}_{\text{p}(25)}$ are one order lower than RMSE of $\text{pH}_{\text{p}(25)}$. The slope of SST is 0.01325 in Eq. (1), which almost agrees with the calculated slope (0.0155) based on the equilibrium equations of the carbonate system under constant TA (DOE, 1994). On the other hand, the sign for Chl should be generally positive for biological processes. In the case of no calcification, DIC decreases with increasing Chl due to photosynthesis, and then pH increases. However, the sign for Chl is negative in Eq. (1). Although the reason for this is uncertain, it may be caused by calcification by the planktonic organisms and corals in the surface ocean. In the case of no photosynthesis, TA decreases with calcification, and then pH decreases. Even if there is negative sign of Chl, our equation could be useful for reconstructing surface pH using SST and Chl over the North Pacific because Eq. (1) has $p < 0.001$ and RMSE 0.025.

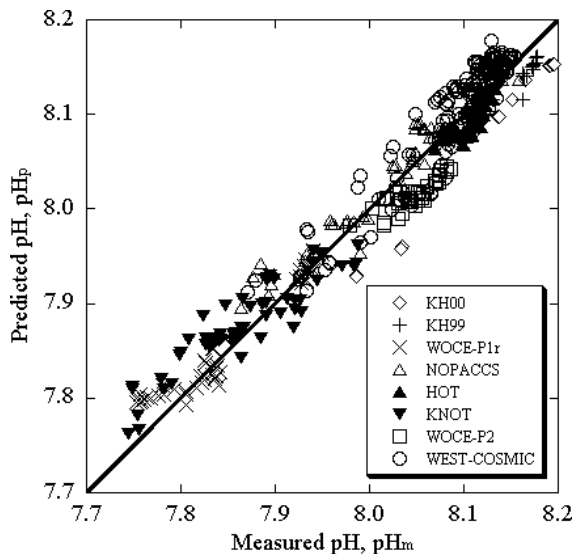


Fig. 2. Plots of the measured pH ($\text{pH}_{\text{m}(25)}$) versus predicted pH ($\text{pH}_{\text{p}(25)}$) in the surface layer of all cruises (0–30 m) based on a linear regression of pH as a function of sea surface temperature (SST, K) and chlorophyll *a* (Chl , $\mu\text{g l}^{-1}$) in the North Pacific. Solid line represents the 1:1 regression line between $\text{pH}_{\text{m}(25)}$ and $\text{pH}_{\text{p}(25)}$. Filled triangles and reverse filled triangles are values in HOT and KNOT, respectively. The other symbols are the same as in Fig. 1.

3.2 Application of the algorithm for the time series stations in the subarctic and subtropical regions

We also have to confirm whether Eq. (1) is useful to determine the temporal change of pH. Thus, we here compare the $\text{pH}_{\text{p}(25)}$ with the $\text{pH}_{\text{m}(25)}$ for two observational time series stations, HOT in the subtropical region and KNOT in the subpolar region (Figs. 3(a) and (b)). To compare $\text{pH}_{\text{p}(25)}$ with $\text{pH}_{\text{m}(25)}$, we estimated the average $\text{pH}_{\text{p}(25)}$ and $\text{pH}_{\text{m}(25)}$ above 30 m at each observation point because not all observations always report the surface $\text{pH}_{\text{m}(25)}$, Chl and SST. In HOT, the $\text{pH}_{\text{m}(25)}$ had an annual variability of 8.069–8.133 pH and the average of ΔpH ($\text{pH}_{\text{m}(25)} - \text{pH}_{\text{p}(25)}$, $n = 33$) is 0.012 ± 0.011 pH. On the other hand, in KNOT, the $\text{pH}_{\text{m}(25)}$ had an annual variability of 7.745–7.988 pH and the average of ΔpH ($n = 19$) is -0.005 ± 0.031 pH. The standard deviation of ΔpH in the subpolar region was larger than that in the subtropical region, which may be caused by the larger biological variability in the subpolar region. For the total of all ΔpH data in the two time series stations from 1992 to 2002, the average ($n = 52$) is 0.006 ± 0.022 pH. If we can find the large difference of ΔpH in both HOT and KNOT, Eq. (1) is inappropriate to reconstruct of pH. However, considering RMSE in our algorithm, we could not find any significant difference of ΔpH at the two stations. Therefore, our equation would be useful to estimate the seasonal variability of pH over

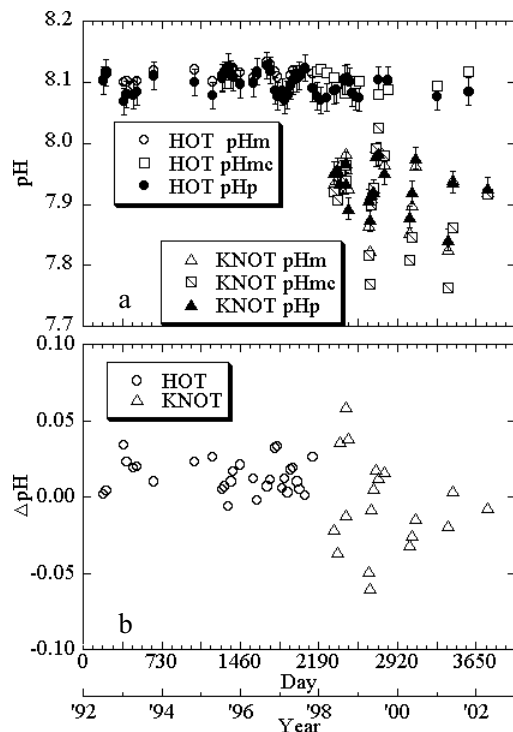


Fig. 3. Comparisons among the measured pH (pH_{m}), the calculated pH (pH_{mc}) from DIC and TA and the predicted pH (pH_{p}) in the surface layer at Station HOT (1992–2001) and Station KNOT (1998–2002). Horizontal axis is the number of Julian days starting from January 1, 1992. We show the average values of pH_{m} , pH_{mc} and pH_{p} above 30 m in the surface layer. The error bars indicate the standard deviations. (a) The pH_{m} (HOT pH_{m} : open circles, KNOT pH_{m} : open triangles), the pH_{mc} (HOT pH_{mc} : open squares, KNOT pH_{mc} : open slash squares) and the pH_{p} (HOT pH_{p} : filled circles, KNOT pH_{p} : filled triangles). (b) The difference between pH_{m} and pH_{p} . The ΔpH ($\text{pH}_{\text{m}} - \text{pH}_{\text{p}}$) in HOT (open circles) and KNOT (open triangles).

the North Pacific.

Moreover, it is necessary to compare $\text{pH}_{\text{m}(25)}$ with the other data set that was not included to obtain Eq. (1). In HOT, we had no data on the pH after 1998 but we had the data sets of DIC and TA. Thus, we calculated the pH from DIC and TA ($\text{pH}_{\text{mc}(25)}$) at 25°C (Fig. 3(a)). The average of $\Delta\text{pH}_{\text{mc}}$ ($\text{pH}_{\text{mc}(25)} - \text{pH}_{\text{p}(25)}$, $n = 15$) is 0.012 ± 0.025 pH, which is the same as ΔpH ($\text{pH}_{\text{m}(25)} - \text{pH}_{\text{p}(25)}$, 0.012) during 1992 to 1997. The standard deviation for the $\Delta\text{pH}_{\text{mc}}$ (0.025) is about twice that of the ΔpH ($\text{pH}_{\text{m}(25)} - \text{pH}_{\text{p}(25)}$, 0.011). However, it is possible that the difference of standard deviations between the $\Delta\text{pH}_{\text{mc}}$ and ΔpH is caused by the error in pH calculated using DIC and TA. In KNOT, we already used pH data during the entire observation period. We also calculated the pH from DIC and TA ($\text{pH}_{\text{mc}(25)}$) at 25°C and we compared the $\text{pH}_{\text{p}(25)}$

Table 2. Parameters used for reconstructing the carbonate species in previous studies and this one. Spatiotemporal restriction means that these algorithms have been divided by seasons and/or oceanic regions. Only the algorithm of pH in this study has no spatiotemporal restriction.

	DIC	TA	$f\text{CO}_2$	pH
SST	○	○	○	○
Salinity	—	○	○	—
Nutrients	○	—	○	—
Chlorophyll- <i>a</i>	—	—	○	○
Spatiotemporal restriction	○	○	○	—

with the $\text{pH}_{\text{mc}(25)}$ in KNOT during 1998 to 2002 (Fig. 3(a)). The average of $\Delta\text{pH}_{\text{mc}}$ ($\text{pH}_{\text{mc}(25)} - \text{pH}_{\text{p}(25)}$, $n = 17$) is 0.026 ± 0.032 pH. The standard deviation of $\Delta\text{pH}_{\text{mc}}$, 0.032 is the same as ΔpH in KNOT ($\text{pH}_{\text{m}(25)} - \text{pH}_{\text{p}(25)}$, 0.031). The average of $\Delta\text{pH}_{\text{mc}}$ (0.026) is different from that of the ΔpH ($\text{pH}_{\text{m}(25)} - \text{pH}_{\text{p}(25)}$, -0.005). However, average of $\Delta\text{pH}_{\text{mc}}$ lies within the standard deviation of 0.032 and might be caused by the larger biological variability in the subpolar region. Moreover, the average of $\Delta\text{pH}_{\text{mc}}$ is possibly influenced by errors in the dissociation constants of carbonic acid and nutrients. Therefore, Eq. (1) could be useful for reconstructing pH in HOT and KNOT over the decade 1992–2002.

Recent studies have reported that DIC had increased by 1 and $2 \mu\text{mol kg}^{-1}\text{yr}^{-1}$ due to the rising atmospheric CO_2 and the change of water ventilation at HOT and KNOT respectively (Winn *et al.*, 1998; Wakita *et al.*, 2005). Assuming TA to be constant, our equation could be useful for detecting the decadal trends of DIC which equated to 0.02–0.04 pH/10 years (DOE, 1994). Thus, our algorithm could be useful for reconstructing pH over the whole North Pacific basin scale during all seasons. Our equation is the first algorithm with no spatiotemporal restriction (Table 2). In this study, we corrected the offsets of pH among the cruises because pH data were measured by two different methods (the spectrophotometric and potentiometric techniques) and according to two different pH scales. In the future, we will have many data of pH by using the spectrophotometric technique. Therefore, the error of our algorithm would be decrease using pH offsets.

Furthermore, we tried to calculate the DIC using the equilibrium equations of the carbonate system from $\text{pH}_{\text{p}(25)}$ and TA fitted to a function of salinity with the equation of Millero *et al.* (1998), and compared the predicted DIC (DIC_{p}) and the measured DIC (DIC_{m}) (Weiss, 1974; Dickson and Millero, 1987; DOE, 1994) (Figs. 4(a) and (b)). The average of ΔDIC ($\text{DIC}_{\text{m}} - \text{DIC}_{\text{p}}$, $n = 47$) is $5.2 \pm 21.8 \mu\text{mol kg}^{-1}$ for both HOT and KNOT. This scatter could be caused by the error of predicted TA and

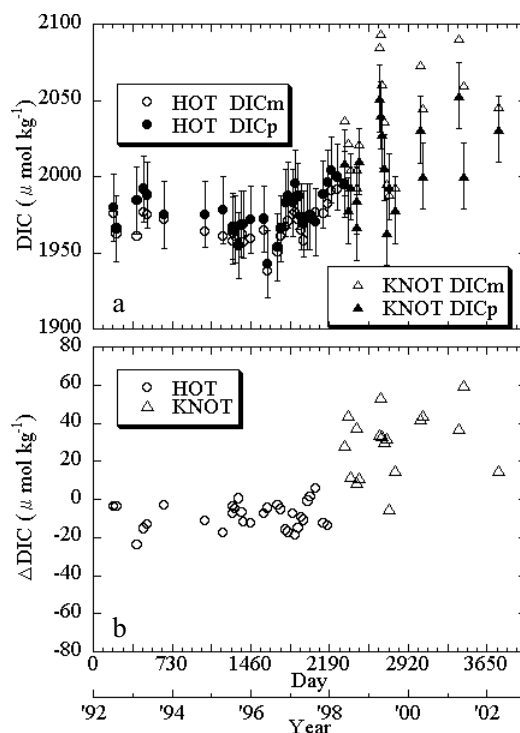


Fig. 4. Comparisons between measured DIC (DIC_{m}) and predicted DIC (DIC_{p}) in the surface layer at Station HOT (1992–1997) and Station KNOT (1998–2002). Horizontal axis is the number of Julian days starting from January 1, 1992. We show the average values of DIC_{m} and DIC_{p} above 30 m in the surface layer. The error bars indicate the standard deviations. (a) DIC_{m} (HOT DIC_{m} : open circles, KNOT DIC_{m} : open triangles) and DIC_{p} (HOT DIC_{p} : filled circles, KNOT DIC_{p} : filled triangles). (b) Difference between DIC_{m} and DIC_{p} , ΔDIC ($\text{DIC}_{\text{m}} - \text{DIC}_{\text{p}}$) at HOT (open circles) and KNOT (open triangles).

$\text{pH}_{\text{p}(25)}$, which is comparable to those in the previous study that calculated the normalized DIC using relationships of salinity-normalized DIC with SST in the North Pacific (Lee *et al.*, 2000).

3.3 Reconstruction of pH at *in situ* temperature

To describe the CO_2 equilibrium system and understand *in situ* physical and biological conditions, it is necessary to correct the $\text{pH}_{(25)}$ back to the pH at the *in situ* seawater temperature ($\text{pH}_{(\text{T})}$). To estimate $\text{pH}_{(\text{T})}$ from $\text{pH}_{(25)}$, we need temperature, salinity, DIC and TA data with $\text{pH}_{(25)}$ (Millero, 1995). Unfortunately, only ship observations can provide these data. Therefore, these observations provide only snapshot data, which might be insufficient for a spatiotemporal description of the pH. In order to obtain $\text{pH}_{(\text{T})}$ without temperature, salinity, DIC and TA, we also developed a $\text{pH}_{(\text{T})}$ algorithm using SST and Chl.

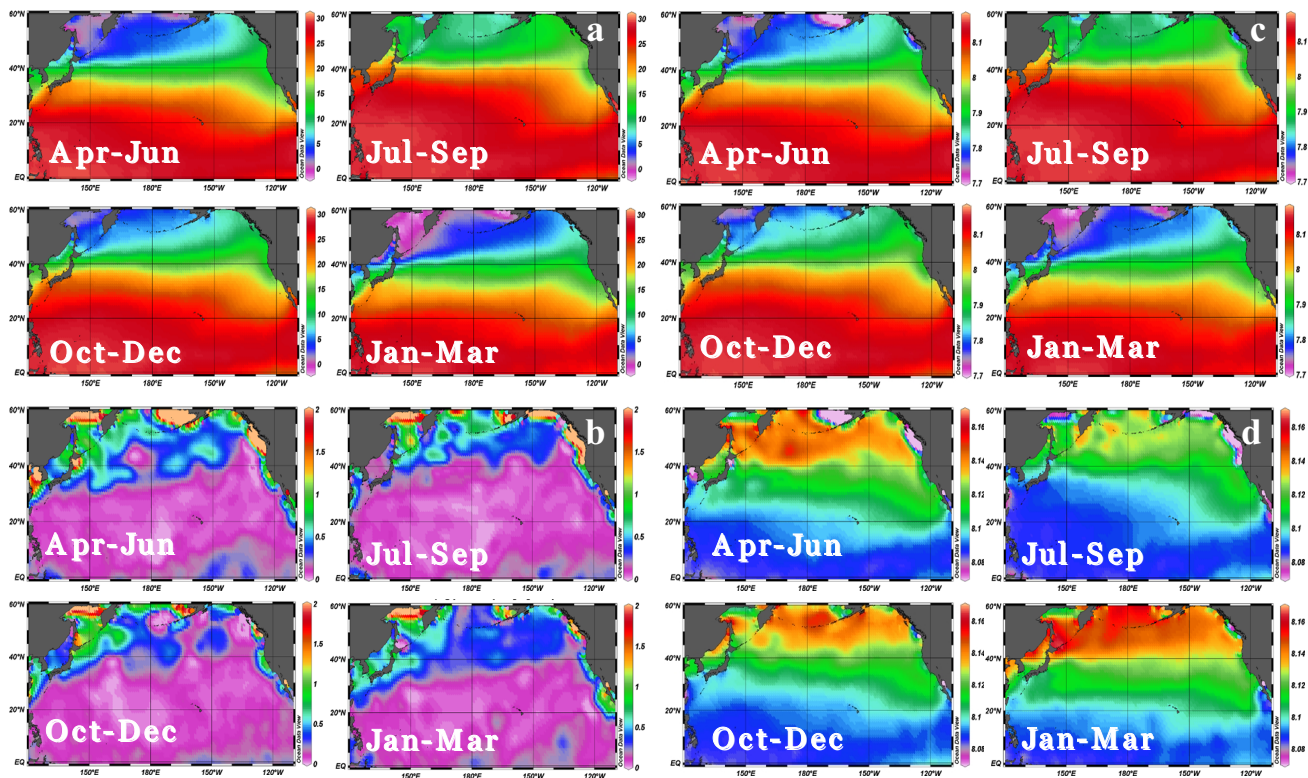


Fig. 5. (a) Distribution of SST (0–30°C) over the North Pacific (0°N–60°N, 120°E–110°W), (WOA 2001). (b) As (a) but for Chl (0–2 $\mu\text{g l}^{-1}$), (WOA 2001). (c) As (a) but for $\text{pH}_{(25)}$ (7.7–8.2 pH) reconstructed using Eq. (1) with SST and Chl. (d) As (a) but for $\text{pH}_{(T)}$ (8.07–8.17 pH) reconstructed using Eq. (3) with SST and Chl.

According to back calculation from $\text{pH}_{(25)}$ to $\text{pH}_{(T)}$ (Millero, 1995), we converted the measured $\text{pH}_{(25)}$ to the $\text{pH}_{(T)}$. We here parameterized the difference between $\text{pH}_{(25)}$ and $\text{pH}_{(T)}$ as functions of SST and Chl.

$$\text{pH}_{(25)} - \text{pH}_{(T)} = 0.01591 \text{ SST} - 0.00101 \text{ Chl} - 4.742 \quad (\text{RMSE} = 0.003, R^2 = 0.99, p < 0.0001, n = 407). \quad (2)$$

In Eq. (2), the differences between $\text{pH}_{(25)}$ and $\text{pH}_{(T)}$ have a strong correlation with both SST and Chl ($p < 0.001$). Substituting Eq. (2) into Eq. (1), we can simply obtain $\text{pH}_{(T)}$ ($\text{pH}_{\text{p}(T)}$) as follows.

$$\text{pH}_{\text{p}(T)} = -0.00266 \text{ SST} - 0.0243 \text{ Chl} + 8.892. \quad (3)$$

Using Eq. (3), we can reconstruct the $\text{pH}_{\text{p}(T)}$ using SST and Chl.

3.4 Reconstruction of pH in the surface seawater over the North Pacific basin using WOA 2001

To describe the spatiotemporal variation of $\text{pH}_{(25)}$ and $\text{pH}_{\text{p}(T)}$ over the North Pacific with our algorithms, we used the four seasons data set (Apr–Jun, Jul–Sep, Oct–Dec and

Jan–Mar) of the World Ocean Atlas (WOA) 2001 (Ocean Climate Laboratory National Oceanographic Data Center, 2002).

In general, the SST increased east-southward north of 40°N and decreased east-northward south of 40°N, i.e., there was a boundary layer near 40°N (Fig. 5(a)). The variation of SST in the winter was larger than that in summer. South of 40°N, we could find hardly any seasonal variation of SST. On the other hand, the Chl generally increased northward and had a high value of 7 $\mu\text{g l}^{-1}$ in the marginal sea. North of 40°N, the seasonal variation of Chl was higher in spring than other seasons with a large variation of 6 $\mu\text{g l}^{-1}$. South of 40°N, we found almost no seasonal variation of Chl (Fig. 5(b)).

The spatiotemporal distributions of $\text{pH}_{\text{p}(25)}$ were similar to those of SST due to the large difference between *in situ* temperature (SST) and 25°C (Figs. 5(a) and (c)). We found that the distribution of $\text{pH}_{\text{p}(25)}$ was almost constant latitudinally. North of 40°N, the $\text{pH}_{\text{p}(25)}$ had a large seasonal amplitude (maximum: 0.5 pH) due to seasonal variation of SST. South of 40°N, we almost found a small seasonal variation of $\text{pH}_{\text{p}(25)}$ (<0.1 pH) due to small variations of both Chl and SST.

The spatiotemporal distribution of $\text{pH}_{\text{p(T)}}$ had a narrower range (8.0–8.2 pH in the open ocean) than $\text{pH}_{\text{p(25)}}$ (7.7–8.2 pH in the open ocean), which agrees with the theoretical equation describing the oceanic carbonate system (Millero, 1995) (Fig. 5(d)). North of 40°N, the seasonal variation of $\text{pH}_{\text{p(T)}}$ (maximum: 0.06 $\text{pH}_{\text{p(T)}}$) was not similar to that of SST because Chl affected $\text{pH}_{\text{p(T)}}$ rather than $\text{pH}_{\text{p(25)}}$ (Figs. 5(a), (b) and (d)). South of 40°N, we almost found no seasonal variation of $\text{pH}_{\text{p(T)}}$ (<0.03 pH). The above spatiotemporal distributions of $\text{pH}_{\text{p(25)}}$ and $\text{pH}_{\text{p(T)}}$ are the first description of pH in surface waters over the North Pacific basin in all seasons.

4. Concluding Remarks

We found a strong correlation between pH, SST and Chl over the North Pacific surface water ($p < 0.0001$). This is the first algorithm to reconstruct spatiotemporal distribution the pH within ± 0.025 pH using a simple equation over the North Pacific. Moreover, our algorithm allowed us to describe the seasonal distribution of sea surface pH over the North Pacific basin using the SST and Chl of WOA 2001.

Some studies have reported a linear increase of water temperature with the changing oceanic physical conditions in the past several decades (Yasuda and Hanawa, 1997; Levitus *et al.*, 2000; Michael and Dongxiano, 2002; Hansen *et al.*, 2002). Several studies have also reported changes in marine biological activity, such as phytoplankton, zooplankton and Chl based on spatiotemporally restricted data sets (Venrick *et al.*, 1987; Falkowski and Wilson, 1992; Sugimoto and Tadokoro, 1997; Karl *et al.*, 2001; Gregg and Conkright, 2002). Satellite measurements have recently reproduced detailed spatiotemporal distribution of SST and Chl. Using the satellite data, our algorithm will allow us to estimate the detailed spatiotemporal distribution of pH over the North Pacific, and to detect the seasonal change and decadal shifts of oceanic condition in the future.

Acknowledgements

Special thanks to Prof. S. Tsunogai and Dr. S. Watanabe for valuable comments and encouragement in the spectrophotometric pH measurement. We thank Dr. Y. Nojiri and Dr. N. Tsurushima for the use of the KNOT data sets. We acknowledge Profs. K. Kuma, T. Ikeda and S. Saitoh, and Drs. N. Shiga and A. Yamaguchi, and the captain, officers and crew of the T/S Oshoro Maru for the offer of Chl data in KNOT. We also thank the many scientists and technicians for assistance with the collection of hydrographic data in the North Pacific and their dedicated work during the long-term observations.

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