Reconciliation of $pH_{25}$ and $pH_{\text{in situ}}$ acidification rates of the surface oceans: A simple conversion using only in situ temperature

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Abstract

Seawater pH is frequently measured at 25°C ($pH_{25}$), and can be converted thermodynamically to pH at the in situ temperature ($T$, $pH_{\text{in situ}}$) using an additional carbonate chemistry parameter, which is the total alkalinity (TA), dissolved inorganic carbon (DIC), or the partial pressure of CO$_2$ (pCO$_2$) of seawater. Although rates of temporal change of $pH_{\text{in situ}}$ ($\beta_{pH_{\text{in situ}}}$) and $pH_{25}$ ($\beta_{pH_{25}}$) are both extensively used in studies of ocean acidification, the difference between $\beta_{pH_{\text{in situ}}}$ and $\beta_{pH_{25}}$ has not yet been quantified. This study deduces from 816 sets of data of the surface oceans over wide ranges of $T$ (1–31°C) from six time series to reveal that the difference between calculated $pH_{\text{in situ}}$ and $pH_{25}$ is $a_1$ ($T - 25°C$), where $a_1$ is a nearly constant of −0.0151 pH unit °C$^{-1}$. We illustrate that $\beta_{pH_{\text{in situ}}}$ equals ($\beta_{pH_{25}} + a_1\beta_T$), where $\beta_T$ is the rate of temporal change of $T$. We further show that uneven distributions of sampling points significantly widen the difference between $\beta_{pH_{\text{in situ}}}$ and $\beta_{pH_{25}}$, making the degree of ocean acidification unclear. Distributions of $a_1$ values are modeled for the surfaces of the global oceans at various pCO$_2$ levels, and they closely match the observations from the studied time series. Without the use of an additional carbonate chemistry parameter, the $pH_{\text{in situ}}$ and $pH_{25}$, as well as $\beta_{pH_{\text{in situ}}}$ and $\beta_{pH_{25}}$, can now be converted into each other using only $T$, facilitating the study of the changing carbonate chemistry of seawater under the influences of increasing atmospheric CO$_2$ concentration.

The pH of seawater reflects directly the state of the acid-base systems of the oceans (Marion et al. 2011). It has attracted much attention recently, as it reflects the seawater acidification of the oceans under the influence of the increasing atmospheric CO$_2$ concentration (Dore et al. 2009; Olafsson et al. 2009; Byrne et al. 2010; Gonzalez-Davila et al. 2010; Ishii et al. 2011; Bates et al. 2014; Lui and Chen 2015; Lui et al. 2015), which has in turn been caused by the fact that since the industrial revolution, humans have released a massive amount of CO$_2$, so-called anthropogenic CO$_2$, to the atmosphere. The global oceans absorb around one third of the anthropogenic CO$_2$, increasing their CO$_2$ concentration but reducing their pH and the saturation state of calcium carbonate through the air-sea CO$_2$ exchange, adversely affecting marine ecosystems (Sabine et al. 2004; Dore et al. 2009; Feely et al. 2009; Olafsson et al. 2009; Bates et al. 2014).

The dissolution of CO$_2$ and the dissociation constants, $K_0$, $K_1$, and $K_2$, can be expressed as follows.

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} &\rightleftharpoons [\text{H}_2\text{CO}_3], \quad K_0 = [\text{H}_2\text{CO}_3]/\text{pCO}_2 \\
[\text{H}_2\text{CO}_3] &\rightleftharpoons [\text{H}^+][\text{HCO}_3^-], \quad K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] \\
[\text{HCO}_3^-] &\rightleftharpoons [\text{H}^+][\text{CO}_3^{2-}], \quad K_2 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-]
\end{align*}
\]

where pCO$_2$ is the partial pressure of CO$_2$.

As shown above, the carbonate system includes five unknowns (pCO$_2$, $[\text{H}_2\text{CO}_3]$, $[\text{H}^+]$, $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$) but only three independent equations. Therefore, the carbonate system can be solved only using an additional pair of four measurable carbonate chemistry parameters—pCO$_2$, pH, dissolved inorganic carbon (DIC) = $[\text{H}_2\text{CO}_3]+[\text{HCO}_3^-]+[\text{CO}_3^{2-}]$, and the total alkalinity (TA) = $[\text{HCO}_3^-]+2[\text{CO}_3^{2-}]+[\text{OH}^-]+[\text{H}^+] + [\text{B(OH)}_4^-]$ + minor bases (Ben-Yaakov 1970; Hunter 1998; Orr et al. 2015). Since the dissociation constants are functions of seawater temperature ($T$) and salinity ($S$), a change in $T$ or $S$ alters the speciation of the carbonate system and therefore the pH value (Ben-Yaakov 1970; Mehrbach et al. 1973; Dickson and Millero 1987; Millero 1995). pH is commonly measured at a constant temperature, such as at the most favored 25°C ($pH_{25}$). The $pH_{25}$ value can then...
be converted thermodynamically to pH at the in situ $T$ ($\text{pH}_{\text{insitu}}$) when the DIC, TA, or pCO$_2$ of seawater has been measured.

The pH$_{25}$ and pH$_{\text{insitu}}$ time series have been used to determine how the oceans respond to the increase in anthropogenic CO$_2$ concentration. Traditionally, the simple-linear-regression (SLR) method has been applied to the pH$_{\text{insitu}}$ or pH$_{25}$ time series. The slopes of the regression lines of the pH$_{\text{insitu}}$ ($\beta_{\text{pH}_{\text{insitu}}}$) and pH$_{25}$ ($\beta_{\text{pH}_{25}}$) time series reflect the rate of temporal change of pH, which is the so-called acidification rate (Dore et al. 2009; Gonzalez-Davila et al. 2010; Midorikawa et al. 2010; Ishii et al. 2011; Bates et al. 2014; Lui and Chen 2015). However, as shall be shown later, the reported $\beta_{\text{pH}_{\text{insitu}}}$ and $\beta_{\text{pH}_{25}}$ may differ significantly. For example, at the Carbon Retention in a Colored Ocean Project (CARIACO) site, reported $\beta_{\text{pH}_{\text{insitu}}}$ values are between $-0.00214$ and $-0.0025$ pH unit yr$^{-1}$ (Astor et al. 2013; Bates et al. 2014), which are about 56% higher than the expected rate of $-0.0017$ pH unit yr$^{-1}$, assuming air-sea CO$_2$ equilibrium. In contrast, the $\beta_{\text{pH}_{25}}$ is just $-0.0004$ pH unit yr$^{-1}$ (Astor et al. 2013), which is 76% lower than obtained by assuming air-sea CO$_2$ equilibrium. The difference between $\beta_{\text{pH}_{\text{insitu}}}$ and $\beta_{\text{pH}_{25}}$, however, has not yet been quantified so reported $\beta_{\text{pH}_{\text{insitu}}}$ and $\beta_{\text{pH}_{25}}$ values are incomparable, making the degree of ocean acidification unclear.

Thermodynamically, the conversion between pH$_{25}$ and pH$_{\text{insitu}}$ is a non-linear function of $T$, $S$, and an additional value of TA, DIC, or pCO$_2$. This study uses 816 time series measurements of the surface seawaters from six stations in the global oceans to show that the difference between calculated pH$_{\text{insitu}}$ and pH$_{25}$ is indeed basically a linear function of $T$. Furthermore, the difference between $\beta_{\text{pH}_{\text{insitu}}}$ and $\beta_{\text{pH}_{25}}$ is shown to be a linear function of the rate of temporal change of $T$ ($\beta_T$). The difference between $\beta_{\text{pH}_{\text{insitu}}}$ and $\beta_{\text{pH}_{25}}$ is shown potentially to be increased by the uneven distributions of the sampling points of the time series. The implications of our findings for studies of changing seawater carbonate systems are discussed.

### Methods and materials

In this study, time series data from six stations in the global surface oceans are analyzed. The stations include the Bermuda Atlantic Time Series Study (BATS, taken from Bates (2007) and http://bats.bios.edu), CARIACO (taken from Astor et al. (2013) and the Institute of Marine Remote Sensing, University of South Florida. http://www.imars.usf.edu/CAR/), European Station for Time Series in the Ocean at the Canary Islands (ESTOC, taken from Gonzalez-Davila and Santana-Casiano (2009)), Hawaii Ocean Time Series (HOT, taken from Dore et al. (2009) and http://www.soest.hawaii.edu/HOT_WOCE/index.php), Kyodo North Pacific Ocean Time-Series (KNOT, taken from Wakita et al. (2010)), and the South East Asia Time-Series Study (SEATS, provided by the Taiwan Ocean Data Bank) (Fig. 1). The up-to-date CO$_2$ System Calculations Program version 2.1, developed by Pierrot et al. (2006), is used to calculate the measureable carbonate chemistry parameters, using recommended dissociation constants for carbonate chemistry that are taken from Lueker et al. (2000) (Dickson et al. 2007; Orr et al. 2015). The pH$_{\text{insitu}}$ at the CARIACO are calculated using the measured pH$_{25}$ and TA data, and the pH$_{\text{insitu}}$ and pH$_{25}$ at the other stations are calculated using the measured TA and DIC data. The $\beta_{\text{pH}_{\text{insitu}}}$, $\beta_{\text{pH}_{25}}$, and $\beta_T$ values are shown in Table 1.

To study the distributions of the changes in pH$_{\text{insitu}}$ with $T$ ($a_1$) at the surfaces of the global oceans, the climatological
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Table 1. Observed surface seawater $\beta_{\text{pH}^{\text{in situ}}}$, $\beta_{\text{pH}25}$, and $\beta_T$ at various time series stations.

| Time series study          | Studied period | $(\times 10^{-3}$ pH unit yr$^{-1}$) | $(\times 10^{-3}$ pH unit yr$^{-1}$) | $\beta_T$ (°C yr$^{-1}$) |
|----------------------------|----------------|-------------------------------------|-------------------------------------|--------------------------|
| BATS (Bates 2007)          | 1983–2005      | $-1.7 \pm 0.3$                       | $-0.4 \pm 0.5$                     | 0.017 ± 0.030            |
| CARIACO (Astor et al. 2013)| 1996–2008      | $-2.5 \pm 0.4$                       | $-0.5 \pm 0.4$                     | 0.09 ± 0.02              |
| (deseasoned)               |                |                                     |                                     |                         |
| CARIACO (Lui and Chen 2015)*| 1995–2010      | $-2.14 \pm 0.37$                     | $-0.74 \pm 0.41$† (This study)     | 0.093 ± 0.034           |
| ESTOC (Santana-Casiano et al. 2007; Gonzalez-Davila et al. 2010) | 1995–2004      | $-1.4 \pm 0.7$                       | $-1.8 \pm 0.3$                    | 0.002 ± 0.019           |
| ESTOC (Lui and Chen 2015)† | 1995–2009      | $-1.84 \pm 0.39$                     | $-1.48 \pm 0.24$† (This study)     | 0.023 ± 0.039           |
| Complete dataset: An extreme case of uneven sampling point distribution: |                | $1.61 \pm 0.37$                      | $-2.53 \pm 0.42$† (This study)     | $-0.273 \pm 0.036$      |
| HOT (Dore et al. 2009)     | 1988–2007      | $-1.9 \pm 0.2$                       | $-1.5 \pm 0.4$                     | 0.026 ± 0.016           |
| KNOT (Wakita et al. 2010)  | 1997–2008      | $-0.26 \pm 1.85$                     | $-0.17 \pm 4.35$                   | 0.00045 ± 0.20          |
| SEATS (Lui and Chen 2015)† | 1998–2006      | $0.206 \pm 1.50$                     | $-3.20 \pm 1.45$† (This study)     | $-0.226 \pm 0.157$      |
| 137°E (Midorikawa et al. 2010) | 1983–2007    | Winter: $-1.8 \pm 0.2$               | Winter: $-1.5 \pm 0.3$             | Winter: 0.02 ± 0.02     |
|                            |                | Summer: $-1.3 \pm 0.5$               | Summer: $-1.4 \pm 0.4$             | Summer: $-0.01 \pm 0.02$ |

*Data taken from the Institute of Marine Remote Sensing, College of Marine Science, University of South Florida. http://www.imars.usf.edu/CAR/.
†Determined with the same dataset shown in Lui and Chen (2015). Data taken from Gonzalez-Davila and Santana-Casiano (2009). Data provided by the Ocean Data Bank (ODB), Ministry of Science and Technology, Taiwan.

monthly $T$, $S$ from the World Ocean Atlas 2001, and the TA data (31,607 data points) estimated using the monthly $T$ and $S$ of the surface oceans, presented in Lee et al. (2006), are used to calculate the $pH_{\text{in situ}}$ and $pH_{25}$ at various pCO$_2$ values using the MATLAB Program developed for CO$_2$ system calculations (version 1.1) (van Heuven et al. 2011). The phosphate and silicate concentrations are assumed to be zero. At each station, the climatological monthly differences between $pH_{\text{in situ}}$ and $pH_{25}$ (Δ$H_{\text{in situ}-25}$) values are plotted vs. the monthly $T$, and $a_1$ is then obtained using the SLR method by forcing the regression line to pass through the reference point ($T = 25\, ^\circ C$, Δ$H_{\text{in situ}-25} = 0$). The $pH_{\text{in situ}}$ and $pH_{25}$ are reported in the total scale. The values in this study are expressed as value ± one standard error.

Results and discussion

Conversions between $pH_{\text{in situ}}$ and $pH_{25}$ and between $\beta_{pH_{\text{in situ}}}$ and $\beta_{pH_{25}}$ using $T$

Figure 2 plots $pH_{\text{in situ}}$ minus $pH_{25}$ (Δ$H_{\text{in situ}-25}$) vs. $T$ at six time series stations. Interestingly, although the seawaters at the studied time series stations have wide ranges of $T$ (1–31°C), $pH_{\text{in situ}}$ (8.002–8.189) and $pH_{25}$ (7.656–8.130), they exhibit almost identical Δ$H_{\text{in situ}-25}$ vs. $T$ linearity. $pH_{25}$ equals $pH_{\text{in situ}}$ when $T$ is at 25°C. The regression reveals that the SLR lines have almost the same slopes, between –0.0150 and –0.0152 pH unit °C$^{-1}$, when they are forced to pass through the reference point at Δ$H_{\text{in situ}-25} = 0$ and $T = 25°C$. The average standard error is just ±0.00036 pH unit (or just ±0.0001 pH unit when the KNOT data is excluded) (Table 2). The slopes are consistent with DeGrandpre et al. (2014)’s calculations of –0.015 pH unit °C$^{-1}$ at the HOT and BATS stations and –0.016 pH unit °C$^{-1}$ for the coastal water in the northeast Pacific Ocean, suggesting the ranges of the slopes (the $a_1$ values) of the surface world oceans are fairly narrow as will be shown and discussed later.

As mentioned, the conversion between $pH_{25}$ and $pH_{\text{in situ}}$ is a non-linear function of $T$, $S$, and an additional value of TA, DIC, or pCO$_2$. Empirically, $pH_{\text{in situ}}$ can be expressed as a non-linear function of $pH_{25}$, $T$, $S$, and the TA/DIC ratio (Millero 1995). In past decades, the TA/DIC ratio has declined insignificantly when $S$ changes only a little (by less than 5, for example) (Millero 1995). Since $S$ values in most parts of the oceans around the world, especially in the case of time series data, vary in a narrow range, the conversion depends on the use of only $T$. Based on the result above, the $pH_{\text{in situ}}$ and $pH_{25}$ among the studied time series can be written as follows.

$$pH_{\text{in situ}} = pH_{25} + a_1(T-25°C),$$  \hspace{1cm} (1)

where $a_1$ is the slope of the plot of Δ$H_{\text{in situ}-25}$ vs. $T$, referring to the amount of $pH_{\text{in situ}}$ change as $T$ increases.

Based on Eq. 1, the conversion between the long-term trends of $pH_{\text{in situ}}$ and $pH_{25}$ can be simplified using a factor...
a_T, and is discussed as follows. To determine the rate of acidification of the oceans, the SLR method has been used to model the long-term temporal changes of pH_{in situ} and pH_{25}. For any pH_{in situ} time series, β_{pH_{in situ}} is defined as follows (Montgomery et al. 2006).

\[
β_{pH_{in situ}} = \frac{\sum_{i=1}^{n} pH_{in situ}(t_i - \bar{t})}{\sum_{i=1}^{n} (t_i - \bar{t})^2},
\]

where pH_{in situ}(i) and t_i are pH_{in situ} and time (t), respectively at t=t_i, and \( \bar{t} \) is the average t.

Substituting Eq. 1 into Eq. 2 yields,

\[
β_{pH_{in situ}} = \frac{\sum_{i=1}^{n} (pH_{25}(t_i - 25)) (t_i - \bar{t})}{\sum_{i=1}^{n} (t_i - \bar{t})^2}
= \sum_{i=1}^{n} pH_{25}(t_i - 25) (t_i - \bar{t})^2 + \sum_{i=1}^{n} T_i (t_i - \bar{t})^2
\]

As \( \sum_{i=1}^{n} pH_{25}(t_i - 25) (t_i - \bar{t})^2 = β_{pH_{25}} \sum_{i=1}^{n} T_i (t_i - 25) (t_i - \bar{t})^2 = β_T \) (see the definition shown in Eq. 2) and \( \sum_{i=1}^{n} (t_i - \bar{t})^2 = 0 \), the above equation can be simplified as follows.

Table 2. Simple linear regression coefficient in Eq. 1 obtained from various time series studies. Value of \( a_1 \) is determined by forcing the regression line to pass through the reference point (ΔpH_{in situ-25} = 0, T = 25°C).

| Station | Year       | \( a_1 \) (pH unit °C⁻¹) | \( R^2 \) | Standard error | n  |
|---------|------------|--------------------------|----------|----------------|----|
| BATS    | 1991–2010  | -0.01519 ± (3.2 × 10⁻⁶)  | 0.999990 | 0.000168       | 215|
| CARIACO | 1995–2010  | -0.01508 ± (2.6 × 10⁻⁶)  | 0.99996  | 0.000070       | 144|
| ESTOC   | 1995–2009  | -0.01516 ± (2.0 × 10⁻⁶)  | 0.99997  | 0.000113       | 144|
| HOT     | 1988–2010  | -0.01515 ± (2.04 × 10⁻⁶) | 0.99996  | 0.000037       | 222|
| KNOT    | 1997–2008  | -0.01504 ± (1.32 × 10⁻⁶) | 0.99998  | 0.001677       | 56 |
| SEATS   | 1998–2006  | -0.01506 ± (4.0 × 10⁻⁶)  | 0.99998  | 0.000075       | 35 |
| Average |            | -0.01511 ± 0.00006       | 0.99989  | 0.000357 ± 0.000648 | Total 816 |
Equation 3 reveals that, mathematically, when $\beta_1$ is a constant, the difference between $\beta_{\text{phnum}}$ and $\beta_{\text{ph25}}$ is $a_1 \beta_T$. Generally, Eq. 1 approximates the thermodynamic effect of $T$ on $\text{pH}_{\text{in situ}}$ and is not affected by biological activities. Therefore, the transformation between $\beta_{\text{phnum}}$ and $\beta_{\text{ph25}}$, the Eq. 3, is also a thermodynamic result, albeit complicated by biological activities. To confirm Eq. 3, observations from six time series (Table 1) present observed $\beta_{\text{phnum}}$, $\beta_{\text{ph25}}$, and $\beta_T$.

$$\beta_{\text{phnum}} = \beta_{\text{ph25}} + a_1 \beta_T + 0$$

$$= \beta_{\text{ph25}} + a_1 \beta_T$$

(3)

Figure 3 plots $\beta_{\text{phnum}}$ vs. $\beta_{\text{ph25}} + a_1 \beta_T$. The result shows that all data, except those at the CARIACO (deseasoned) and the ESTOC sites, fall on the 1 : 1 line, validating our proposed Eq. 3. The deviations at the CARIACO and ESTOC sites arise from statistical errors since their $T$ time series do not have the same sampling distributions as $\text{pH}_{\text{in situ}}$ and $\text{pH}_{25}$. Based on Eq. 3, a direct comparison between $\beta_{\text{phnum}}$, $\beta_{\text{ph25}}$, and $\beta_T$ yields a difference of $a_1 \beta_T$. Worth mentioning, the datasets used in this study cover wide ranges of $T$ (1–31°C), $\text{pH}_{\text{in situ}}$ (8.002–8.189), $\text{pH}_{25}$ (7.656–8.130), TA (2167–2673 μmol kg$^{-1}$), DIC (1859–2389 μmol kg$^{-1}$), as well as normalized TA (NTA = TA/S × 35, 2252–2534 μmol kg$^{-1}$) and DIC (NDIC = DIC/S × 35, 1928–2251 μmol kg$^{-1}$) values. Although five of the time series stations have stable NTA concentrations, those at CARIACO show large temporal variations (2252–2534 μmol kg$^{-1}$). That is, our proposed Eqs. 1 and 3 are applicable over a wide $T$, $\text{pH}_{\text{in situ}}$, $\text{pH}_{25}$, NTA (or TA), and NDIC (or DIC) ranges. The distributions of $a_1$ values of the surface oceans will be shown and discussed later.

Uneven distributions of sampling points increase differences between $\beta_{\text{phnum}}$ and $\beta_{\text{ph25}}$

From Eq. 3, the difference between $\beta_{\text{phnum}}$ and $\beta_{\text{ph25}}$ is $a_1 \beta_T$, where $a_1$ is almost a constant and is between $-0.0150$ and $-0.0152$ pH unit °C$^{-1}$ in the six time series (Fig. 2). That is, the difference between $\beta_{\text{phnum}}$ and $\beta_{\text{ph25}}$ increases with increasing $\beta_T$. Using ESTOC as an example, Lui and Chen (2015) showed an extreme example of uneven sampling distributions that the sampling time gradually shifts from summer to winter. The result was that the $\beta_T$ changed from $0.023 \pm 0.039°$C yr$^{-1}$ (complete dataset) to $-0.273 \pm 0.036°$C yr$^{-1}$ (Table 1).

Figure 4 shows that although the observed $\beta_{\text{phnum}}$ and $\beta_{\text{ph25}}$ at the six stations and 137 °E line varied greatly, the differences between $\beta_{\text{phnum}}$ and $\beta_{\text{ph25}}$ are negatively correlated with $\beta_T$. All data, except for those at the CARIACO (deseasoned) and the ESTOC sites, fall on the $-0.0151 \beta_T$ line, and the $-0.0151$ pH unit °C$^{-1}$ is the average $a_1$ value among the six time series (Table 2). As mentioned, the slight deviations at the CARIACO and ESTOC sites arise from statistical
errors since their $T$ time series do not have the same sampling distributions as $\text{pH}_{\text{insitu}}$ and $\text{pH}_{25}$. Generally speaking, the $\beta_T$ that is caused by global warming is only about $-0.01^\circ C$ yr$^{-1}$ (Karl et al. 2015), so the large range of the observed $\beta_T$ values is caused largely by the uneven sampling distribution. The above illustrates that uneven distributions of sampling points increase the differences between $\beta_{\text{pH}_{\text{insitu}}}$ and $\beta_{\text{pH}_{25}}$. In that case, either $\beta_{\text{pH}_{\text{insitu}}}$ and $\beta_{\text{pH}_{25}}$ contain the deviations due to the uneven sampling distributions. Using our proposed method, $\text{pH}_{\text{insitu}}$ and $\text{pH}_{25}$ data, as well as their rates of temporal changes now can transform to each other using only $T$. This helps avoiding the confusion in evaluating the acidification rate using $\text{pH}_{\text{insitu}}$ or $\text{pH}_{25}$ data. We suggest that long-term monthly or seasonal sampling strategy efficiently helps reducing the deviations of $\beta_{\text{pH}_{\text{insitu}}}$ and $\beta_{\text{pH}_{25}}$ due to the uneven sampling distributions. In the case of short-term and unevenly distributed time-series data, the use of an appropriate regression model may help reducing the deviations. In the cases that $\text{pH}_{\text{insitu}}$ and $\text{pH}_{25}$ time series can be expressed empirically as functions of $t$ and $T$, the deviations of $\beta_{\text{pH}_{\text{insitu}}}$ and $\beta_{\text{pH}_{25}}$ due to the uneven sampling distributions can be largely removed using the multiple linear regression method with $t$ and $T$ as variables (Lui and Chen 2015).

**Global distributions and estimations of $a_1$**

Figure 5 plots the distributions of the modeled $a_1$ values using the climatological monthly $T$ (−2 to 32°C), $S$ (31–38) and estimated TA data (2053–2494 μmol kg$^{-1}$), taken from Lee et al. (2006), for pCO$_2$ values of 280 ($\text{pH}_{\text{insitu}}$: 8.139–8.188, $\text{pH}_{25}$: 7.739–8.260), 400 ($\text{pH}_{\text{insitu}}$: 8.004–8.063, $\text{pH}_{25}$: 7.610–8.140) and 800 ($\text{pH}_{\text{insitu}}$: 7.720–7.813, $\text{pH}_{25}$: 7.362–7.891) μatm. The use of different color scales is to show the small regional differences of the $a_1$ values at various pCO$_2$ levels. The results reveal that although the surface ocean has various physical and chemical properties, it has very similar $a_1$ values, ranging from $-0.0152$ to $-0.0153$ (average $-0.01529$ ± 0.00003) pH unit $^\circ C^{-1}$, when pCO$_2$ = 280 μatm. The $a_1$ values decrease and the regional differences of $a_1$ values increase as pCO$_2$ increases. When pCO$_2$ is 400 μatm, the $a_1$ values are slightly lower, at between $-0.01510$ and $-0.01482$ (average: $-0.01502$ ± 0.00005) pH unit $^\circ C^{-1}$. At a pCO$_2$ of 800 μatm, the $a_1$ values are between $-0.01456$ and $-0.01357$ (average $-0.0141$ ± 0.000285) pH unit $^\circ C^{-1}$. The observed $a_1$ values of $-0.01504$ to $-0.01519$ pH unit $^\circ C^{-1}$, shown in Fig. 2, match closely the modeled $a_1$ values when pCO$_2$ is between 280 μatm and 400 μatm, validating the modeled results in Fig. 5. Generally speaking, the $a_1$ value is a function of $T$, $S$ and a pair of TA, DIC, pCO$_2$, and $\text{pH}_{\text{insitu}}$ or $\text{pH}_{25}$. Therefore, to state the applicable ranges of each carbonate parameter for our proposed method is complicated. The above information provides a reference of their applicable ranges.

Although $a_1$ declines as pCO$_2$ increases, the value changes little as pCO$_2$ varies between pre-industrial and present levels. As shown in Fig. 5 and Table 2, $a_1$ is approximately $-0.0151$ between 50°N and 50°S, and it is about $-0.0150$ pH unit $^\circ C^{-1}$ at higher latitudes. Notably, based on the assumption that the uncertainty in $a_1$ is ±0.00036 pH unit $^\circ C^{-1}$ (or just ±0.0001 when KNOT is excluded) pH unit $^\circ C^{-1}$, a transformation of a $\text{pH}_{25}$ value to $\text{pH}_{\text{insitu}}$ at $T$ as low as 0°C yields an uncertainty of only $(± 0.00036 \times 25)$ = ±0.009 pH unit. The uncertainty is less when $T$ is closer to 25°C. Therefore, even lacking an additional carbonate parameter, historical $\text{pH}_{\text{insitu}}$ or $\text{pH}_{25}$ data for the surface ocean can still be converted to each other using only $T$ and $a_1$, which has been shown to be close to $-0.0151$ pH unit.
C−1. When the $K_1$ and $K_2$ values that are taken from Lueker et al. (2000) are used, the average $a_1$ of the studied time series is $-0.01511 \pm 0.00006$ pH unit C−1. When the corresponding values from Mehrbach et al. (1973), refitted by Dickson and Millero (1987), and from Millero (2010), are used, $a_1$ becomes $-0.01492 \pm 0.0001$ and $-0.01492 \pm 0.00007$ pH unit C−1, respectively. The differences between such values are approximately 0.0002 pH unit C−1. Therefore, equilibrium constants should be used consistently in all calculations to prevent an additional, albeit small, systematic error.

**Conclusions**

The conversion between pH25 and pHinsitu traditionally requires an additional carbonate parameter. This study reveals that only T and a coefficient, $a_1$ which is about $-0.0151$ pH unit C−1, are required to convert linearly pH25 and $p_{\text{H}^+}_{\text{insitu}}$ to pHinsitu and $p_{\text{H}^+}_{\text{insitu}}$, respectively, and vice versa. This study demonstrates that the conversion between pH25 and $p_{\text{H}^+}_{\text{insitu}}$ can be significantly enlarged owing to uneven distributions of sampling points. Our method is applicable over wide T, pHinsitu, pH25 and NTA ranges, facilitating the study of the changing carbonate chemistry of seawater, such as to avoid the confusion in evaluating the acidification rate using pHinsitu or pH25 data.

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Conflict of Interest

None declared.

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