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Deducing acidification rates based on short-term time series

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We show that, statistically, the simple linear regression (SLR)-determined rate of temporal change in seawater pH (β_{pH}), the so-called acidification rate, can be expressed as a linear combination of a constant (the estimated rate of temporal change in pH) and SLR-determined rates of temporal changes in other variables (deviation largely due to various sampling distributions), despite complications due to different observation durations and temporal sampling distributions. Observations show that five time series data sets worldwide, with observation times from 9 to 23 years, have yielded β_{pH} values that vary from 1.61×10^{-3} to -2.5×10^{-3} pH unit yr^{-1} . After correcting for the deviation, these data now all yield an acidification rate similar to what is expected under the air-sea CO_2 equilibrium (-1.6×10^{-3} ~ -1.8×10^{-3} pH unit yr^{-1}). Although long-term time series stations may have evenly distributed datasets, shorter time series may suffer large errors which are correctable by this method.

Ocean acidification is an unavoidable consequence of increasing atmospheric CO_2 ¹⁻⁵. Understanding how fast the oceans acidify is critical to examining and predicting the impact of ocean acidification on the aquatic ecosystem. Invaluable decadal ocean time series measurements of carbonate chemistry parameters can now be used for this purpose. Observations show that surface ocean pH under *in situ* temperature ($\text{pH}_{\text{insitu}}$) has strong seasonal variations, with a high $\text{pH}_{\text{insitu}}$ in winter and a low $\text{pH}_{\text{insitu}}$ in summer. Long-term decreasing trends are superimposed on the regular seasonal variations⁶⁻⁸.

To investigate how fast the oceans acidify, the widely used first-order simple linear regression (SLR) method has been used to model the long-term temporal changes in $\text{pH}_{\text{insitu}}$ (β_{pH})^{2,6-13}. The SLR model in general form is as follows,

$$\text{pH} = \text{pH}^\circ + \beta_{pH}t, \quad (1)$$

where pH° is the intercept, β_{pH} is the slope, and t is time in the $\text{pH}_{\text{insitu}}$ vs. t plot.

The β_{pH} , the so-called acidification rate, refers to an average rate of temporal change in $\text{pH}_{\text{insitu}}$. Conventional wisdom has it that the longer the $\text{pH}_{\text{insitu}}$ time series (e.g., over a decade) the better the estimation of the β_{pH} . Bermuda Atlantic Time Series Study (BATS) and the Hawaii Ocean Time Series (HOT) (see Fig. 1 for the station locations) are two examples of long-term time series with even sampling distribution, and their β_{pH} values fairly reflected the acidification rates due to the increased atmospheric CO_2 concentrations^{6,7}. However, in a time series with short observation years (e.g., less than a decade), the small long-term temporal change in $\text{pH}_{\text{insitu}}$ due to the increase in atmospheric CO_2 could be easily masked by the strong seasonal variations, especially in the case of uneven sampling distribution. The $\text{pH}_{\text{insitu}}$ and seawater temperature (T) time series at the European Station for Time Series in the Ocean Canary Islands (ESTOC) between 1995–2009 are shown as examples (Fig. 2). The raw data (blue cross), when fitted by the SLR, result in a negative β_{pH} of $-1.84 \pm 0.39 \times 10^{-3}$ pH unit yr^{-1} and positive SLR-determined rate of temporal change in T (β_T) of $0.023 \pm 0.039^\circ\text{C yr}^{-1}$ (Fig. 2). The red circles represent an extreme example of uneven sampling distribution, with the sampling time gradually shifting from summer to winter. As a result, these data now would have a positive β_{pH} of $1.61 \pm 0.37 \times 10^{-3}$ pH unit yr^{-1} and a negative β_T of $-0.273 \pm 0.036^\circ\text{C yr}^{-1}$. Moreover, the slopes of the regression lines would

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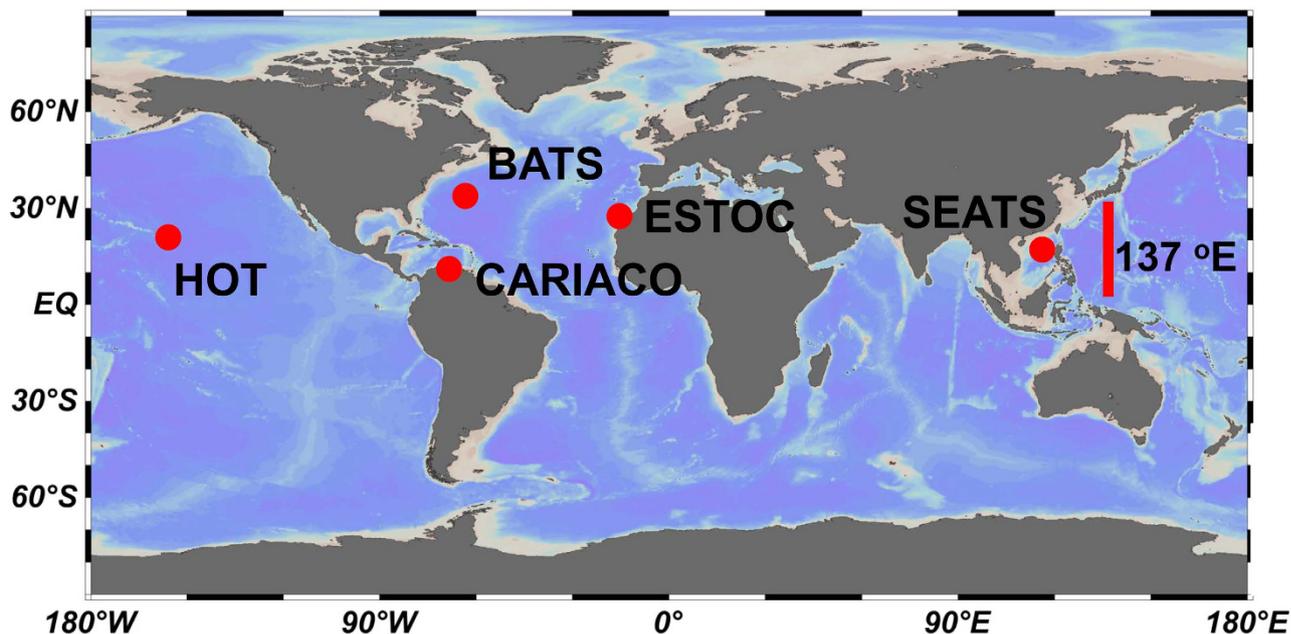


Figure 1. Station locations of the time series, including Bermuda Atlantic Time Series Study (BATS), Carbon Retention in a Colored Ocean Project (CARIACO), European Station for Time Series in the Ocean Canary Islands (ESTOC), Hawaii Ocean Time Series (HOT), South East Asia Time Series Study (SEATS), and 137°E repeated hydrographic line (137°E). The map was generated using Ocean Data View 4.6.2. Schlitzer, R., Ocean Data View, odv.awi.de, 2015.

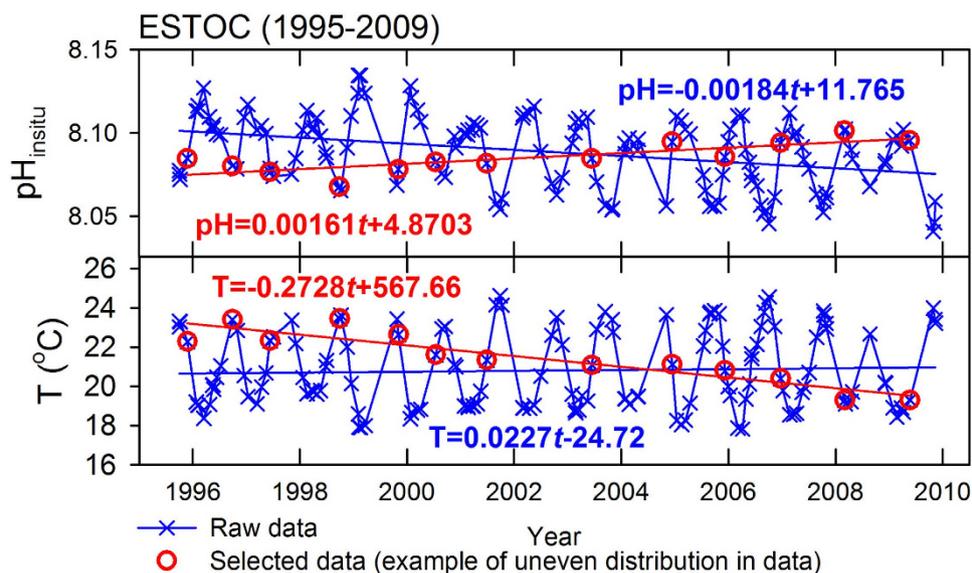


Figure 2. Time series of $\text{pH}_{\text{insitu}}$ and T at ESTOC. The blue crosses and lines show the raw data and the regression lines. The red circles and lines show a case of selected data, and the regression lines. Data taken from Gonzalez-Davila and Santana-Casiano¹⁹.

increase with a shift in sampling time from summer to winter within a shorter observation period. This shows that β_{pH} is highly sensitive to the temporal distribution, and the duration, of time series data.

It has been suggested that the effect of seasonal variations on β_{pH} could largely be reduced when pH anomaly data (observed data minus seasonal average) are used². However, this method may not be applicable to time series with short observation periods and uneven sampling distribution, which do not have sufficient data to generate effective seasonal means, resulting in errors. Furthermore, the reported low values of the coefficient of determination (R^2), ranging from 0.09 to 0.55, indicate that these time

series data were still poorly fitted by SLR lines². Consequently, estimating β_{pH} using only t introduces a deviation due to the influence of strong temporal variations. As a result, it remains unclear whether the observed rates at which surface seawater pH_{insitu} changes differ are due to the changing carbonate chemistry of seawater at different time series stations or to deviation using SLR.

In this study, we propose a simple statistical method for reducing deviations of β_{pH} under the influence of strong temporal variations. We show that when pH is expressed as a linear function of t and the other variables, β_{pH} can be expressed as a linear combination of a constant (an estimated rate of temporal change in pH) and SLR-determined rates of temporal changes in the selected variables (deviation largely due to various sampling distributions under the strong seasonal pH variability), despite complications due to different observation durations and temporal sampling distributions. Using this method, we demonstrate that β_{pH} differs from the observations from five time series stations (the BATS, Carbon Retention in a Colored Ocean Project (CARIACO), ESTOC, HOT, and the South East Asia Time Series Study (SEATS, with bottom depth >3700m)) mainly due to deviations under various sampling distributions rather than changing seawater chemistry. Average summer and winter β_{pH} values from 31 stations along the 137°E repeated hydrographic line (137°E) likely contain the same deviation.

There are few reported acidification rates for the world's oceans, as there are only a handful of stations with decadal time series of carbonate parameters. Time series studies with high temporal variations and few observation years can benefit from our approach to find the fair estimation in the rate of temporal change in pH_{insitu} .

Results

Decomposition of β_{pH} and its physical meaning. Statistically, for any pH_{insitu} time series, β_{pH} is defined as follows¹⁴,

$$\beta_{pH} = \frac{\sum_{i=1}^n pH_i(t_i - \bar{t})}{\sum_{i=1}^n (t_i - \bar{t})^2}, \quad (2)$$

where pH_i and t_i are pH and t , respectively at $t = t_i$, and \bar{t} is the average t .

As t can only be used to model the linear temporal change in pH_{insitu} , it cannot be used to model the strong seasonal variations. Suppose that other variables (e.g. T , dissolved oxygen, nutrients), x_1, \dots, x_n , are added to model the temporal variations in pH_{insitu} , which can be expressed as follows,

$$pH = pH^\circ + m_1(t - t^\circ) + m_2(x_2 - x_2^\circ) + \dots + m_k(x_k - x_k^\circ), \quad (3)$$

where $m_1 \sim m_k$ are constants, t° is a reference point of t , and $x_2^\circ \sim x_k^\circ$ are $x_2 \sim x_k$ at $t = t^\circ$, respectively.

Substituting Eq (3) into Eq (2), Eq (2) can be rewritten as follows,

$$\begin{aligned} \beta_{pH} &= \left(\frac{\sum_{i=1}^n (pH^\circ + m_1(t_i - t^\circ) + m_2(x_{2i} - x_2^\circ) + \dots + m_k(x_{ki} - x_k^\circ))(t_i - \bar{t})}{\sum_{i=1}^n (t_i - \bar{t})^2} \right) \\ &= \left(pH^\circ \frac{\sum_{i=1}^n (t_i - \bar{t})}{\sum_{i=1}^n (t_i - \bar{t})^2} + \left(m_1 \frac{\sum_{i=1}^n t_i(t_i - \bar{t})}{\sum_{i=1}^n (t_i - \bar{t})^2} + m_2 \frac{\sum_{i=1}^n x_{2i}(t_i - \bar{t})}{\sum_{i=1}^n (t_i - \bar{t})^2} + \dots + m_k \frac{\sum_{i=1}^n x_{ki}(t_i - \bar{t})}{\sum_{i=1}^n (t_i - \bar{t})^2} \right) \right. \\ &\quad \left. - \left(m_1 t^\circ \frac{\sum_{i=1}^n (t_i - \bar{t})}{\sum_{i=1}^n (t_i - \bar{t})^2} + m_2 x_2^\circ \frac{\sum_{i=1}^n (t_i - \bar{t})}{\sum_{i=1}^n (t_i - \bar{t})^2} + \dots + m_k x_k^\circ \frac{\sum_{i=1}^n (t_i - \bar{t})}{\sum_{i=1}^n (t_i - \bar{t})^2} \right) \right) \end{aligned}$$

As $\sum_{i=1}^n (t_i - \bar{t}) = 0$ and $\sum_{i=1}^n t_i(t_i - \bar{t}) = \sum_{i=1}^n (t_i - \bar{t})^2$, the equation above can be simplified as follows,

$$\begin{aligned} \beta_{pH} &= m_1 + m_2 \left(\frac{\sum_{i=1}^n x_{2i}(t_i - \bar{t})}{\sum_{i=1}^n (t_i - \bar{t})^2} \right) + \dots + m_k \left(\frac{\sum_{i=1}^n x_{ki}(t_i - \bar{t})}{\sum_{i=1}^n (t_i - \bar{t})^2} \right) \\ &= m_1 + m_2 \beta_{x_2} + m_3 \beta_{x_3} + \dots + m_k \beta_{x_k}, \end{aligned} \quad (4)$$

where $\beta_{x_2} \sim \beta_{x_k}$ are SLR-determined rates of temporal changes in $x_2 \sim x_k$, respectively (see the definition shown in Eq (2)).

Equation (4) shows that in fact, β_{pH} can be expressed as a linear combination of a constant (m_1) and rates of temporal changes in the other regression variables ($m_2 \beta_{x_2} \sim m_k \beta_{x_k}$). Thus, although differences in the number of observation years and temporal distribution of sampling yield different β_{pH} and $\beta_{x_2} \sim \beta_{x_k}$ values for $\beta_{x_2} \sim \beta_{x_k}$ change with β_{pH} , whereas m_1 remains unchanged. Statistically, if $x_2 \sim x_k$ in the above equation have no long-term trends of changes, $\beta_{x_2} \sim \beta_{x_k}$ are expected to be zero. Non-zero $\beta_{x_2} \sim \beta_{x_k}$ refers to the consequence of various sampling distributions under seasonal variations in $x_2 \sim x_k$. If the long-term trends of changes in $x_2 \sim x_k$ have no collinearities with that of pH_{insitu} , any long-term trends of changes in $x_2 \sim x_k$ would not affect β_{pH} .

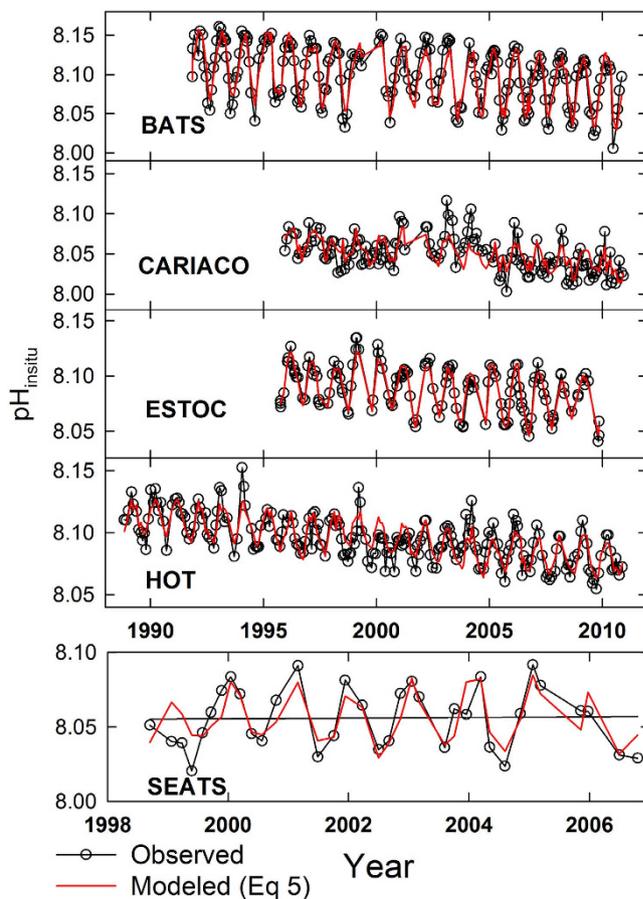


Figure 3. The surface seawater $\text{pH}_{\text{insitu}}$ at various time series stations. The black and red lines show, respectively, the observed values and the values modeled by Eq (5).

Notably, m_1 is defined as the amount of $\text{pH}_{\text{insitu}}$ change as t changes. Therefore, if long-term changes in $\beta_{x_2} \sim \beta_{x_k}$ do not vary with that of t or $\text{pH}_{\text{insitu}}$, m_1 refers to the estimated rate of temporal change in $\text{pH}_{\text{insitu}}$ due to different physical and biological forcings (e.g. changes in anthropogenic CO_2 concentration, productivity, microbial respiration rate, etc.), whereas $m_2 \beta_{x_2} \sim m_k \beta_{x_k}$ refers to the deviation due to the temporal variation. Notably, the deviation due to uneven sampling distribution under strong temporal variations can be quantified using rates of temporal changes in other variables.

Verifications and criteria of additional regression variables. To verify Eq (4), additional variables need to be added to the regression model shown in Eq (3). These variables must be strong in seasonal variations and weak in long-term changes, so that they can be used to model the seasonal variations in the $\text{pH}_{\text{insitu}}$. At the same time they should have weak collinearities with t . Seawater T may serve this purpose, as $\text{pH}_{\text{insitu}}$ is related to T and observations show that the T time series routinely mirrors the $\text{pH}_{\text{insitu}}$ time series^{6,7}. Furthermore, modelled results from recent studies show that the surface ocean $\text{pH}_{\text{insitu}}$ has no observable change under a long-term change in T ^{15,16}.

To verify the appropriateness of using t and T in modeling $\text{pH}_{\text{insitu}}$, Eq (3) is simplified as follows,

$$\text{pH} = \text{pH}^\circ + m_1(t - t^\circ) + m_2(T - T^\circ), \quad (5)$$

where T° is T when $t = t^\circ$.

Using the initial year of $t^\circ = 1988$ as a reference, the multiple linear regression (MLR) model of Eq (5) is then applied to the surface ocean $\text{pH}_{\text{insitu}}$ from five time series stations. The results are shown in Fig. 3 and Table 1.

Linearity between $\text{pH}_{\text{insitu}}$, t , and T . Figure 3 shows the observed $\text{pH}_{\text{insitu}}$ time series and the modeled results using MLR at various time series stations. The regression results match well with the annual, interannual, and long-term variations in observations. The m_1 and m_2 of $-1.6 \pm 0.1 \times 10^{-3} \text{ pH unit yr}^{-1}$ and $-8.7 \pm 1.4 \times 10^{-3} \text{ pH unit } ^\circ\text{C}^{-1}$, respectively, are similar among the time series stations. The R^2 values are increased from $0.09 \sim 0.55$ to $0.51 \sim 0.94$, with all sites averaging 0.75 ± 0.17 . The differences between the measured and the MLR results are at most approximately twice the pH calculation error of

		Eq (5) $\text{pH} = \text{pH}^\circ + m_1(t-t^\circ) + m_2(T-T^\circ)$						
Station	Year	pH°	T°	$m_1 \times 10^{-3} \text{pH unit yr}^{-1}$	$m_2 \times 10^{-3} \text{pH unit } ^\circ\text{C}^{-1}$	Standard Error	R^2	n
BATS	1991–2010	8.1297	22.85	-1.8 ± 0.2	-9.9 ± 0.3	0.0135	0.86	215
CARIACO	1995–2010	8.0835	24.82	-1.5 ± 0.3	-7.0 ± 0.7	0.0155	0.51	144
ESTOC	1995–2009	8.1155	20.46	-1.6 ± 0.1	-9.6 ± 0.2	0.0053	0.94	144
HOT	1988–2010	8.1172	24.68	-1.7 ± 0.1	-9.3 ± 0.5	0.0088	0.77	222
SEATS	1998–2006	8.0531	30.63	-1.5 ± 0.9	-7.7 ± 1.0	0.0123	0.66	35
Average		8.0998 ± 0.0311	24.69 ± 3.76	-1.6 ± 0.1	-8.7 ± 1.4	0.011 ± 0.004	0.75 ± 0.17	5

Table 1. MLR coefficients of Eq (5) of seawater $\text{pH}_{\text{insitu}}$ from various time series studies. The pH° and T° are determined using the SLR method when $t^\circ = 1988$ (see Supplementary Table S2).

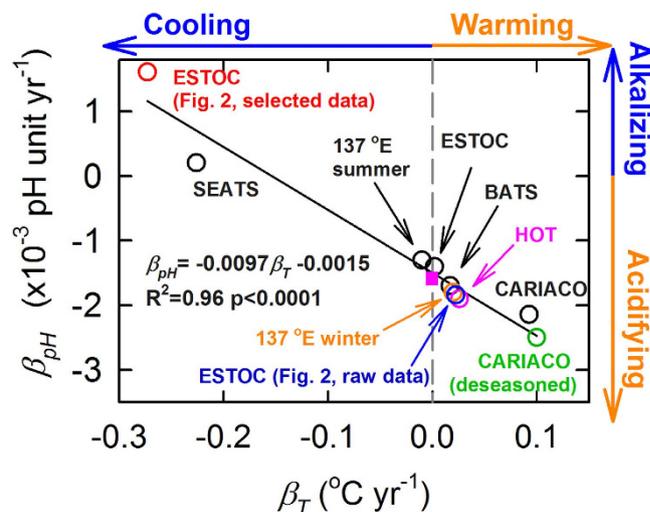


Figure 4. The observed surface seawater β_{pH} vs. β_T at various time series stations. The solid line shows the linear regression result. The pink solid square shows the expected acidification rate based on the assumption of air-sea CO_2 equilibrium. The vertical dashed line represents zero β_T . See the text for the names of the time series studies.

± 0.0062 , based on the carbonate system using total alkalinity (TA) and dissolved inorganic carbon¹⁷, suggesting the validation of Eq (5). Consequently, Eq (4) can now be simplified as follows,

$$\beta_{\text{pH}} = m_1 + m_2\beta_T \quad (6)$$

It is important to point out that the linearity between $\text{pH}_{\text{insitu}}$ and T is a lump sum of various physical and biological forcings. Based on this linearity, the change in β_{pH} due to various sampling distributions under the strong seasonal variability is reflected in $m_2\beta_T$. The fact is that, changes in $\text{pH}_{\text{insitu}}$ and T owing to other factors (e.g. global warming, enhanced upwelling, etc.) may not equal to m_2 , resulting in residuals. The standard errors of Eq (5) shown in Table 1 possibly reflect the errors from minor disturbances and from the measurements. Since Eq (6) is generated from Eq (5), Eq (6) contains the same kind of errors as Eq (5) does. Fortunately, the standard errors are relatively small. Therefore, m_1 is the estimated rate of temporal change in $\text{pH}_{\text{insitu}}$, and $m_2\beta_T$ is the deviation largely due to the various sampling distributions under the strong seasonal $\text{pH}_{\text{insitu}}$ variability. In addition, any parameter, having linearity with $\text{pH}_{\text{insitu}}$ and having no observable temporal collinearities with t or $\text{pH}_{\text{insitu}}$, can technically be used in the same way as T does to quantify the deviation of β_{pH} due to various sampling distributions under strong seasonal $\text{pH}_{\text{insitu}}$ variability.

Linearity between β_{pH} vs. β_T and the deviation ($m_2\beta_T$). To quantify Eq (6), observations from five time series with varying numbers of observation years (9–23 years) are examined with the average β_{pH} of 31 time series stations along the 137°E line in the winter and summer (Fig. 4; detailed information are shown in Supplementary Information Table S1). Determined by SLR on the observed $\text{pH}_{\text{insitu}}$ and T time series, the results show that the observed β_{pH} values vary from $+1.61 \times 10^{-3} \text{pH unit yr}^{-1}$

to -2.5×10^{-3} pH unit yr^{-1} . The slope (m_2) of the regression line of $-9.7 \pm 0.7 \times 10^{-3}$ pH unit $^{\circ}\text{C}^{-1}$ is consistent with the MLR determined m_2 , with an average of $-8.7 \pm 1.4 \times 10^{-3}$ pH unit $^{\circ}\text{C}^{-1}$ for the five time series (Table 1). Although no reported average values in m_1 and m_2 are given, the result in Fig. 4 shows that the average β_{pH} values at the 137 $^{\circ}\text{E}$ likely have m_1 and m_2 values similar to that of the other five time series.

Assuming an air-sea CO_2 equilibrium, the surface ocean has slight regionally distributed differences in acidification rates owing to differences in seawater carbonate chemistry¹⁸. Based on thermodynamic calculations using the average carbonate parameters at each station, the acidification rate among the five time series stations and the 137 $^{\circ}\text{E}$ line are similar between -1.6×10^{-3} and -1.8×10^{-3} pH unit yr^{-1} . As β_{pH} is negatively correlated with β_T , the deviation ($m_2\beta_T$) is equal to zero when β_T is zero. Indeed, the regression line in Fig. 4 yields a β_{pH} of $-1.5 \pm 0.1 \times 10^{-3}$ pH unit yr^{-1} at $\beta_T = 0$. This value agrees with the MLR-determined m_1 of $-1.6 \pm 0.1 \times 10^{-3}$ pH unit yr^{-1} , and with the expected acidification rate of $-1.6 \times 10^{-3} \sim -1.8 \times 10^{-3}$ pH unit yr^{-1} , when considering only the observed global atmospheric pCO_2 increments during the studied periods. Notably, the assumed, extreme case of uneven sampling distribution shown in Fig. 2 agrees well with the regression line (Fig. 4, red circle). As shown for the first time, and having the shortest observation years and the largest deviation from the expected acidification rate (positive β_{pH}), the SEATS site is used as an example to illustrate the influence of sampling distribution on the β_{pH} in the following discussion. At the SEATS site, the observed β_{pH} , m_2 , and β_T of the nine year study are 0.21×10^{-3} pH unit yr^{-1} , -7.7×10^{-3} pH unit $^{\circ}\text{C}^{-1}$, and $-0.23^{\circ}\text{C yr}^{-1}$, respectively (Fig. 4, Table 1). It is important to note that the estimated rate of temporal change in $\text{pH}_{\text{in situ}}$ (m_1) is $\beta_{\text{pH}} - m_2\beta_T = (0.21 \times 10^{-3} \text{ pH unit yr}^{-1}) - (-7.7 \times 10^{-3} \text{ pH unit } ^{\circ}\text{C}^{-1}) \times (-0.23^{\circ}\text{C yr}^{-1}) = -1.6 \times 10^{-3}$ pH unit yr^{-1} , which is statistically indistinguishable from the expected acidification rate, assuming the air-sea CO_2 equilibrium.

Discussion

The results above show that the β_{pH} among the studied time-series, at $\beta_T = 0$, reflects the increasing atmospheric CO_2 , while deviations from that value are mainly due to different deviations of $m_2\beta_T$ under various distributions of sampling points in the studied areas. In short, β_{pH} at ESTOC with only selected data (an extreme case of uneven sampling distribution), and at SEATS and CARIACO, deviates so much from the expected acidification rate due to increasing atmospheric CO_2 , because of the deviation indicated by the apparent decrease in the observed T at ESTOC and SEATS (positive deviation) and the apparent increase in T at CARIACO (negative deviation). The long-term time-series, such as BATS and HOT, have the β_{pH} statistically indistinguishable from the expected rate of $-1.6 \times 10^{-3} \sim -1.8 \times 10^{-3}$ pH unit yr^{-1} assuming air-sea CO_2 equilibrium. That is, although long-term time series may have evenly distributed datasets and negligible deviations in β_{pH} , shorter time series may suffer large errors which are correctable by this method.

It has been suggested that the anomaly (observed $\text{pH}_{\text{in situ}}$ or T minus climatology mean) be used to reduce seasonal variations, as it has been reported that β_{pH} is sensitive to these². Comparing deseasoned β_{pH} from Bates, *et al.*² and deseasoned β_T from Astor, *et al.*⁹, based on $\text{pH}_{\text{in situ}}$ and T anomalies at the CARIACO site, the deseasoned β_{pH} is similar to the observed β_{pH} that contains a deviation of $m_2\beta_T$ (Fig. 4, green circle). The reason why the β_{pH} and the deseasoned β_{pH} contain similar deviations needs further investigation.

The observed slope of $-9.7 \pm 0.7 \times 10^{-3}$ pH unit $^{\circ}\text{C}^{-1}$ shown in Fig. 4 can only be due to changing seawater chemistry, and not to deviations, if the following two conditions are satisfied. First, β_T is a fair estimation of changing T . Second, the change in $\text{pH}_{\text{in situ}}$ under long-term change in T is equal to the m_2 of $-9.7 \pm 0.7 \times 10^{-3}$ pH unit $^{\circ}\text{C}^{-1}$. However, the second assumption contradicts with our thermodynamic calculation that the change in $\text{pH}_{\text{in situ}}$ as T changes (m_2) is in fact just approximately -1.1×10^{-3} pH unit $^{\circ}\text{C}^{-1}$, which is based on the assumptions of air-sea CO_2 equilibrium and constant TA. This is consistent with recent studies showing that the change in surface ocean $\text{pH}_{\text{in situ}}$ under long-term change in T (m_2) is close to zero^{15,16}. Seasonal changes in T are much larger than long-term changes in T , such that the observed m_2 of $-8.7 \pm 1.4 \times 10^{-3}$ and $-9.7 \pm 0.7 \times 10^{-3}$ pH unit $^{\circ}\text{C}^{-1}$ shown in Table 1 and Fig. 4, respectively, largely represents the values of seasonal change in $\text{pH}_{\text{in situ}}$ as T changes. Notably, uneven sampling generates a deviation in β_T as well. Although deducing the deviation in β_T under uneven sampling distribution is beyond the scope of this study, this does not change a fact that based on Eq (6), in the case of uneven distribution of sampling the slope of β_{pH} vs. β_T plot should be approximately equal to $m_2 = -8.7 \pm 1.4 \times 10^{-3}$ pH $^{\circ}\text{C}^{-1}$. In contrast, the slope of fair estimation is expected to be just about -1.1×10^{-3} pH unit $^{\circ}\text{C}^{-1}$. The factor of $-9.7 \pm 0.7 \times 10^{-3}$ β_T shown in Fig. 4 is actually a deviation of the acidification rate largely owing to various distributions of sampling points, rather than an effect on the acidification rate due to warming or cooling.

In the marine carbonate system, the TA concentration should remain constant if the change in $\text{pH}_{\text{in situ}}$ is solely caused by the air-sea CO_2 exchange. To examine the temporal change in the TA concentration, it is normalized to a particular salinity (S), such as at $S = 35$ ($\text{nTA} = \text{TA}/S \times 35$), to reduce the influences of precipitation or evaporation on the TA concentration. At the ESTOC and the 137 $^{\circ}\text{E}$ line, the nTA concentrations have reportedly remained unchanged over the study regions and periods^{8,12}. The rates of temporal change in nTA (β_{nTA}) among the rest of the four sites are also found to be insignificant within the uncertainties of the data (see Supplementary Table S1 for detail). Further, changes in TA

through precipitation or evaporation have insignificant influences on β_{pH} among those time series stations. For instance, at the HOT site, a change in TA as S changes (11×10^{-3} S unit yr^{-1}) yields a β_{pH} of only 0.091×10^{-3} pH unit yr^{-1} . Such a magnitude of change is less than 5% of the reported β_{pH} at the HOT site. In fact, the constant nTA among the studied time series leads to the conclusion that m_1 of -1.6×10^{-3} pH unit yr^{-1} in Table 1 and -1.5×10^{-3} pH unit yr^{-1} in Fig. 4 indeed reflect the increasing atmospheric CO_2 concentration.

To conclude, long-term time series with even sampling distribution contains negligible deviation. However, a short duration of observation years, low sampling frequency, and high seasonal variations in the $\text{pH}_{\text{in situ}}$ time series tend to result in a temporal change with a large deviation. For instance, due to its high seasonal variation in $\text{pH}_{\text{in situ}}$ and short duration, in the SEATS study, the temporal increase in $\text{pH}_{\text{in situ}}$ due to uneven distributions of data is large enough to compensate for decreasing $\text{pH}_{\text{in situ}}$ caused by increased atmospheric CO_2 . T is used as an example to quantify the deviation. Once the deviation is eliminated, seawaters at the studied stations are acidified at a rate statistically indistinguishable from the expected rate under the air-sea CO_2 equilibrium. Our results indicate that the differences in β_{pH} among the studied time series are due to deviations using SLR. As our approach is not so limited by the number of observation years or the sampling distribution, time series studies with high seasonal variations and short duration times can benefit from our approach, achieving a fair estimation of the rate of temporal change in $\text{pH}_{\text{in situ}}$.

Methods

The data sets (see Fig. 1 for station locations) used in this study are from five published time series studies (the BATS⁶, CARIACO^{2,9}, ESTOC^{8,19}, HOT⁷, and the 137°E¹²) and an unpublished, open access pH time series study (the SEATS). In this study, the up-to-date CO_2 System Calculations Program (version 2.1) developed by Pierrot, *et al.*²⁰ and the recommended dissociate constants of carbonate chemistry for best practices^{21,22} were used to calculate the carbonate system. The pH is in the total scale at the *in situ* temperature. Numbers are expressed as the value \pm one standard error.

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Author Contributions

H.K.L. and C.T.A.C. contributed equally to this work. H.K.L. and C.T.A.C. wrote the manuscript text and H.K.L. prepared figures 1–4 and supplementary figure S1. All authors reviewed the manuscript.

Additional Information

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