OS21C-1598 Acidification of the North Pacific Ocean: Direct Observations of pH in 1991 and 2006

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Abstract

Spectrophotometric procedures were first successfully used to obtain seawater pH profiles on a 1991 cruise within the CLIVAR/CO2 Repeat Hydrography Program. During a 2006 reoccupation of the P16N transect along 152°W, closely similar methods were used to obtain a fifteen-year spectrophotometrically-based record of ocean pH change.

Spectrophotometric procedures are particularly robust as a means of observing changes in seawater pH because sulfonephthalein equilibrium constants, being nearly constant at constant temperature and salinity, are unimportant in pH difference calculations. In such cases, the quality of pH difference measurements is most closely related to measurement precision. Since the precision of spectrophotometric pH measurements (using observations of sulfonephthalein absorbance ratios) is on the order of 0.0004 pH units, pH differences can be measured with a precision somewhat better than +/- 0.001. In the absence of other effects, the atmospheric pCO2 increase between 1991 and 2006 would decrease the pH of the surface ocean, in equilibrium with the atmosphere, by approximately 0.025 pH units. Thus, spectrophotometric pH observations are capable of directly resolving pH perturbations on a scale commensurate with potential atmospherically-induced changes.

At depths between 3000 and 5000 meters the directly observed mean fifteen-year pH difference was on the order of 0.000 +/-0.0015. At depths below 1000 meters, pH changes generally ranged between + 0.006 and -0.006. In contrast, in the upper 700 meters, pH was much more variable, with an average fifteen-year pH decrease on the order of 0.025 and including pH differences as large as -0.055. These directly observed pH differences are consistent with expected changes in response to elevated atmospheric CO2, along with differences that can be attributed to changes in respiration and ocean circulation.

Introduction

Since the 1980s approximately 30% of the CO2 released to the atmosphere through human activities has entered the oceans (Sabine et al., 2004). Upon entering the surface ocean, through the reactions

$$CO_2(aq) + H_2O \xrightarrow{K_1} HCO_3^- + H^+ \quad \text{and} \quad (1)$$

$$CO_2(g) \xrightarrow{K_0} CO_2(aq) \quad , \quad (2)$$
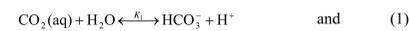
CO2 is predominantly converted to HCO_3^-, the principal dissolved form of inorganic carbon in seawater. Through the acidification reaction shown in equation 2, measurable seawater pH changes are expected in a relatively short time scale. Changes in ocean pH in response to rising atmospheric CO2 can be modeled quantitatively in terms of the total alkalinity of seawater (TA), the pCO2 of seawater, and the buffering contributions of bicarbonate, carbonate, borate, hydroxide, and more minor seawater buffers. As a first-order approximation, neglecting all alkalinity terms other than bicarbonate, TA can be written in terms of pCO2 and pH (where pH = $\log[H^+]^{-1}$) in the form

$$TA \sim K_0 K_1 [H^+]^{-1} pCO_2 \quad . \quad (3)$$

Since TA is constant on long time scales, the relationship between seawater pH and pCO2 at observation times 1 and 2 can be written as

$$(TA)_2 /(TA)_1 = 1 = ([H^+]_2^{-1} / [H^+]_1^{-1}) ((pCO_2)_2/(pCO_2)_1), \quad (4)$$

whereupon

$$\log ((pCO_2)_2/(pCO_2)_1) = pH_1 - pH_2 = \Delta pH. \quad (5)$$

Equation 5 indicates that a doubling of seawater pCO2 will result in a pH change on the order of 0.3 pH units. For an observed pCO2 change on the order of 6% over the past fifteen years, the predicted decrease in surface ocean pH is approximately 0.025 pH units.

Changes of this magnitude are easily discernable via precise spectrophotometric measurement techniques. Comparisons of pH obtained along 152° W in the North Pacific Ocean in 2006 and in 1991 (shortly after the development of quantitative spectrophotometric seawater pH measurement procedures) constitute the longest-duration record of ocean basin pH changes documented using precise spectrophotometric procedures.

Principle of pH measurements
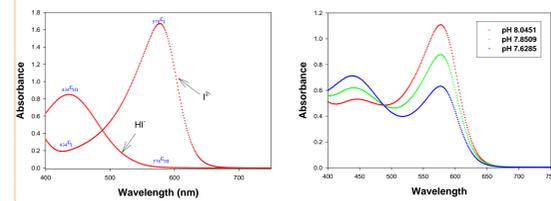
Fig. 1. Spectra of I²⁻ and HI⁻ forms of mCP

Fig. 2. Spectra of mCP in seawater (S=35, t= 25.0°C)

Solution pH can be measured by observation of dissolved substances that are in exchange equilibrium with H^+. Sulfonephthalein indicators, such as meta cresol purple (mCP), are suitable for spectrophotometric pH observations because the protonated (HI^-) and unprotonated (I^{2-}) forms of mCP are strongly colored. For the equilibrium

$$HI^- \xrightleftharpoons{K_I} H^+ + I^{2-} \quad \text{where} \quad (6)$$
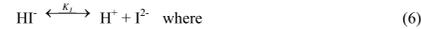
$$K_I = \frac{[H^+][I^{2-}]}{[HI^-]} \quad , \quad (7)$$

solution pH can be written as

$$pH = -\log[H^+] = -\log K_I + \log \frac{[I^{2-}]}{[HI^-]} \quad . \quad (8)$$

The concentrations ([ ]) of HI^- and I^{2-} in equation 8 can be expressed directly in terms of the absorbances ($_\lambda A$) of each species at the absorbance maxima of HI^- ($\lambda=434$ nm) and I^{2-} ($\lambda=578$nm)

$$_{434}A_{HI} = _{434}\epsilon_{HI}[HI^-] \quad (9)$$

$$_{578}A_I = _{578}\epsilon_I[I^{2-}] \quad (10)$$

where $_{434}\epsilon_{HI}$ and $_{578}\epsilon_I$ are molar absorptivities of HI^- and I^{2-} at $\lambda=434$ nm and $\lambda= 578$ nm.

Combining equations 8 through 10, it can be shown (Clayton and Byrne, 1993) that solution pH can be directly measured through observations of mCP absorbance ratios (R=$_{578}A/_{434}A$),

$$pH = -\log K_I' + \log \frac{R - e_1}{e_2 - Re_3} \quad (11)$$

where

$$e_1 = \frac{_{578}\epsilon_{HI}}{_{434}\epsilon_{HI}}, \quad e_2 = \frac{_{578}\epsilon_I}{_{434}\epsilon_{HI}}, \quad e_3 = \frac{_{434}\epsilon_I}{_{434}\epsilon_{HI}} \quad . \quad (12)$$

Fig. 3. pH duplicates along P16N (2006). The vertical axis shows the difference between the pH of duplicate 1 minus the pH of duplicate 2

Replicate measurements obtained along P16N in 2006 are shown in Figure 3. The precision for a single measurement, calculated from 66 paired measurements was on the order of ±0.0009 pH units.

The molar absorbance ratios given in equation 12 are obtained from observations of mCP absorbances at high pH (Figure 1) where the indicator is exclusively present in solution as I^{2-}, and at sufficiently low pH (Figure 1) that the indicator is predominantly present as HI^-. The absorbance ratio R in equation (11) is directly obtained through observations of mCP absorbances in natural seawater (Figure 2). Seawater pH on the total hydrogen ion concentration scale is then calculated as

$$pH = pK_1 + \log\left(\frac{R - 0.0069}{2.2220 - 0.1331R}\right) \quad \text{and} \quad (13)$$

$$pK_1 = 1245.69/T + 3.8275 + 0.00211(35-S) \quad (14)$$

where R is the measured absorbance ratio, T is Kelvin temperature and S is salinity.

All shipboard pH measurements in this work were obtained at T=298.15°K. As such, it should be noted that, for small salinity variations between paired pH measurements (2006 and 1991), pK_1 is very nearly constant. In this case pH differences (ΔpH) can be written simply as

$$\Delta pH = \Delta \log\left(\frac{R - 0.0069}{2.2220 - 0.1331R}\right) \quad . \quad (15)$$

Measurements of pH at sea were obtained by adding mCP to seawater samples in thermostatted 10-cm pathlength spectrophotometric cells to achieve concentrations on the order of 3 micromolar. Absorbances were corrected for baseline changes via absorbance measurements at a non-absorbing wavelength (730 nm). Absorbance ratios were calculated from absorbances measured at 578 nm and 434 nm. Small corrections were made for variations in the purity of mCP obtained from different vendors. These corrections ranged from approximately 0.004 pH units at pH 8.0 to 0.001 at pH 7.2. Seawater pH is then calculated using equations 13 and 14.

Results

Fig. 4. Seawater pH distributions along 152°W in 2006

Distributions of pH observed in 2006 along 152°W are shown in figure 4A, left panel (21.5°N to 45°N) and 4B, right panel (45°N to 56.2°N). At depths below 5000 m along the transect, pH ranged between 7.57 and 7.60. Surface water pH south of 45°N ranged between 7.9 and 8.1. North of 45°N, surface pH values ranged between approximately 7.7 and 7.9. Minimum pH values south of 45°N were observed near 1000 meters. North of 45°N, minimum pH values shoaled to approximately 200 meters and included values as low as pH 7.2.
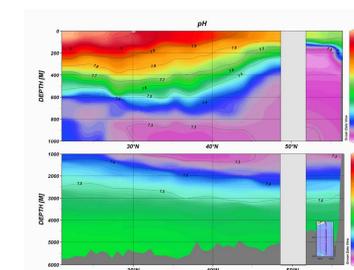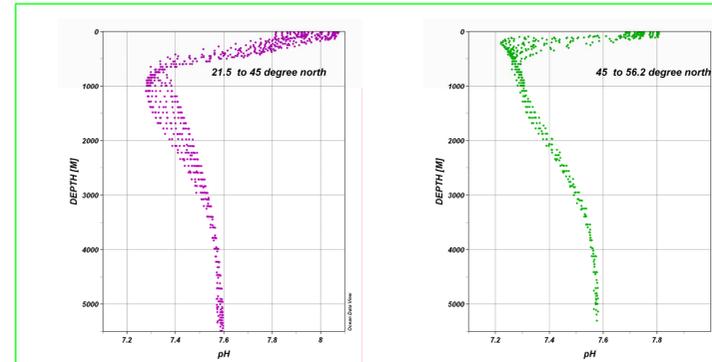
Fig. 5. pH along 152°W (1991)
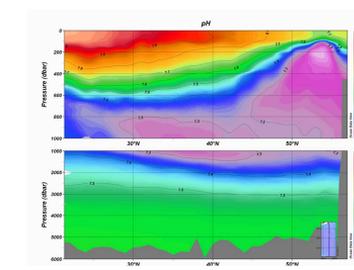
Fig. 6. pH along 152°W (2006)

Contour plots of pH are shown in Figures 5A and 5B for 1991 and in Figures 6A and 6B for 2006. Extremely sharp pH gradients, and therefore gradients in carbonate saturation state, are observed near 53°N at depths shallower than 150 meters. The pH distributions in Figures 4, 5 and 6 closely resemble water-column distributions of AOU (Apparent Oxygen Utilization).

Fig. 7. pH difference (pH₂₀₀₆–pH₁₉₉₁) along 152°W

Figure 7 shows pH differences along 152°W between 1991 and 2006. Differences were calculated by comparing pH values (1991 and 2006) along isopycnal surfaces. Differences were then plotted vs. latitude and depth. Insignificant pH differences are observed below approximately 600 meters. At depths shallower than 500 meters, a pronounced decrease in pH is observed between 1991 and 2006 at most latitudes. At depths above 500 m, ΔpH ranges between 0 and -0.05 pH units with average values on the order of -0.025±0.02. No positive ΔpH values are seen at depths shallower than 700 m.

Fig. 8. AOU difference (AOU₂₀₀₆–AOU₁₉₉₁) along 152°W

The ΔAOU plot shown in Figure 8 suggests that some of the changes shown in Figure 7 are due to variations in physical ventilation processes (Mecking et al., 2006) — in particular much of the large decrease in pH seen along σ_θ = 26.6 kg m⁻³ is associated with a large increase in AOU. The maximum ΔAOU changes shown in Figure 7 (ΔAOU ~ 25 μmol/kg) are consistent (through Redfield ratio variations in O2, DIC and TA) with respiration-induced changes in pH on the order of -0.047. However, such effects, induced by changes in circulation rates, are limited in spatial extent. For example, Δ AOU anomalies at depths between the surface and 100 m are largely absent in Figure 8, while ΔpH values (Figure 7) range between -0.02 to -0.03.

Fig. 9. Computed ΔTA between 2006 and 1991

The ΔpH variations shown in Figure 7 are consistent with observed increases in DIC along P16N. Figure 9 shows a cross section of ΔTA (2006-1991) calculated from 2006 and 1991 measurements of both the DIC and pH. Calculations were obtained via the CO2sys program developed by Lewis and Wallace (http://cdiac.ornl.gov/oceans/co2rprt.html) using the carbonate constants of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987). Calculations accounted for the contributions of nutrient buffers such as silicate and phosphate.

The ΔTA observations shown in Figure 9 are generally close to zero (-15≤ΔTA≤10 μmol kg⁻¹). This figure indicates that the observed pH changes shown in Figure 7 are dominantly attributable to observed changes in DIC between 1991 and 2006.

Fig.10. ΔpH signal attributable to the ΔAOU signals shown in Figure 8.

Figure 10 shows changes in pH attributable to ΔAOU via variations in O2, DIC and TA.

Through the modified Redfield biomass respiration reaction (Anderson and Sarmiento, 1994),

$$(CH_2O)_{117}(NH_3)_{16}(H_3PO_4) + 170 O_2$$

$$\xrightarrow{respiration} 117CO_2 + 133H_2O + 16NO_3^- + H_2PO_4^- + 17H^+ \quad ,$$

respiration of one mole of O2 causes DIC to increase by 117/170 moles and, through production of H^+, causes a decrease in TA of 17/170 moles. These changes in DIC and TA both contribute to a decrease in seawater pH.

Fig. 11. ΔpH signal from anthropogenic CO2 along P16N between 2006 and 1991

Figure 11 shows the ΔpH signal along P16N corrected for the ΔAOU-induced pH changes shown in Figure 10. The ΔpH signals shown in Figure 11 provide a first-order account of pH changes that are solely attributable to oceanic uptake of anthropogenic CO2. The ΔpH signal in the upper 500 meters of Figure 11 ranges between approximately -0.04 and -0.01 with a mean near -0.02.

Conclusions

Due to increasing atmospheric CO2, the pH of seawater in exchange equilibrium with the atmosphere is predicted to have decreased by as much as 0.025 pH units between 1991 and 2006.

Directly observed pH differences (2006-1991) along 152°W in the North Pacific at depths shallower than 500 m are similar in magnitude to changes (ΔpH ~ -0.025±0.02) predicted from a chemical equilibrium model.

Between 1991 and 2006, pH changes along 152°W are quantitatively consistent with observed changes in DIC at approximately constant alkalinity.

Ocean circulation changes also contribute to the pH changes observed in the North Pacific along 152°W between 1991 and 2006. Changes in pH attributable to changes in physical mixing shown in Figure 8 are not as spatially extensive as directly observed pH changes (Figure 7) that are attributable to the combined effects of circulation change and CO2 exchange with the atmosphere.

References

Anderson L.A. and Sarmiento J.L. (1994) Redfield ratios of remineralization determined by nutrient data analysis. *Global Biogeochem. Cycles* **8**, 65-80.
Clayton T.D. and Byrne R.H. (1993) Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. *Deep-Sea Research* **40**, 2115-2129.
Dickson A. G., and Millero F. J . (1987) A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Research* **34**,1733-1743.
Mecking S., Warner M.J. and Bullister J.L. (2006) Temporal changes in pCFC-12 ages and AOU along two hydrographic sections in the eastern subtropical North Pacific. *Deep-Sea Research* I **53**, 169-187.
Mehrbach C., Culberson C. H., Hawley J. E. and Pytkowicz R. M. (1973) Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnology and Oceanography* **18**, 897-907.
Sabine C.L., Feely R.A., Gruber N., Key R.M., Lee K., Bullister J.L., Wanninkhof R., Wong C. S., Wallace D.W. R., Tilbrook B., Millero F.J., Peng T.H., Kozyr A, Ono T., Rios A.R. (2004) The Oceanic sink for anthropogenic CO2. *Science*, **305**, 367 – 371.