

SURFACE pH OF THE NORTHEASTERN PACIFIC OCEAN

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ABSTRACT

A latitudinal, differential pH distribution is observed in the Northeastern Pacific Ocean with a pH range of 8.15 at high latitude ($42^{\circ}N$) to 8.29 at low latitude ($23^{\circ}N$). These pH values are generally greater than the calculated equilibrium pH with respect to atmospheric carbon dioxide. If we assume that the calculated equilibrium pH values are valid, then the surface waters are undersaturated with respect to the atmospheric carbon dioxide during April to June 1966. A high surface pH value of about 8.26 was observed immediately south of the Subarctic Boundary zone near $170^{\circ}W$. This value differs from the equilibration pH by as much as 0.1 unit.

INTRODUCTION

On the basis of oceanic variables, such as temperature and salinity, the pH at the surface of the ocean, away from the shore, should have some correlation with latitude. Indeed, a certain correlation was observable in the cruise data of R/V *Vityaz* and R/V *Ob*, 1957-1958, of the Moscow Oceanological Institute (Postma 1964). When surface pH is compared with the equilibrium pH with respect to the atmospheric carbon dioxide, one can study the direction of the air-sea exchange of carbon dioxide qualitatively. Recently we have studied the latitudinal dependency of the surface pH in the Northeastern Pacific Ocean. We report our findings here.

OBSERVATIONS

Water samples were analyzed aboard R/V

Yaquina during her *Yaloc 66* cruise. Fig. 1 shows the stations occupied for this study. In order to show the latitudinal pH trend, the NE-SW line of the stations between Oregon and Hawaii (series "A") and SE-NW line between Hawaii and the Aleutians (series "B") are discussed in this report. The series "A", $22^{\circ}25' - 41^{\circ}24'N$, was studied during 23 April-9 May 1966, and the series "B", $22^{\circ}54' - 52^{\circ}08'N$, during 31 May-28 June 1966.

The pH was measured by a method described in the manual of Strickland and Parsons (1965). The procedure for collecting water samples from Nansen bottles was exactly the same for pH measurements as for oxygen measurements. Special care was given to allow no air space in the samples. After samples were placed in a constant temperature bath, $25^{\circ}C$, for several minutes, the pH was measured by dipping a

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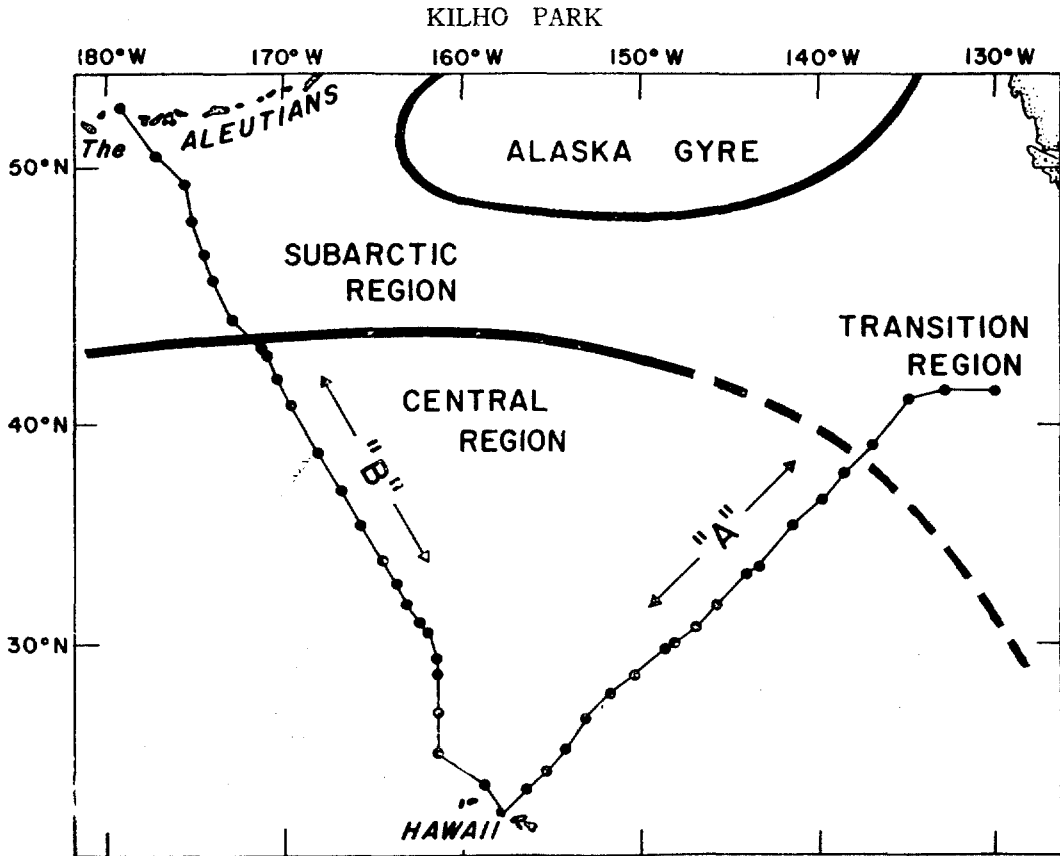


Figure 1. Stations occupied for the surface pH study. Various zonings of the Northeastern Pacific is after Fleming (1955).

pair of glass and calomel electrodes directly in the 120-ml capacity polypropylene bottles (Fig. 2). A Beckman pH meter, Model 7600, expanded scale, was used to measure the pH values.

RESULTS

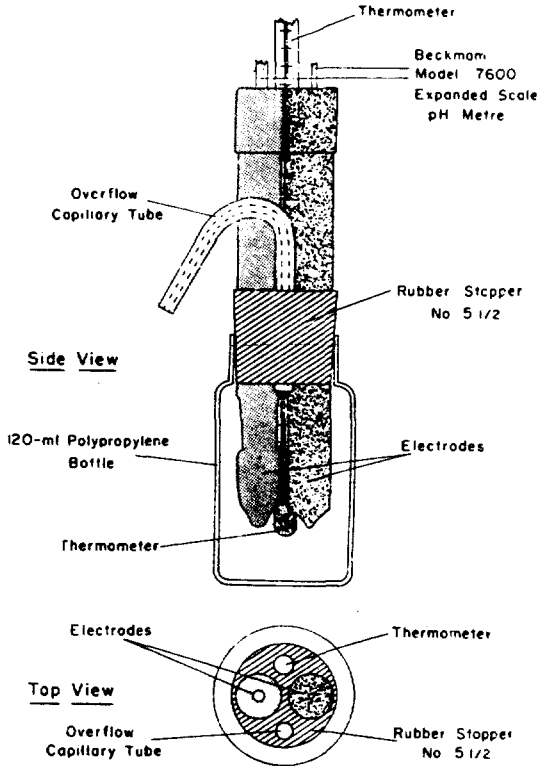
The upper parts of Fig. 3 and 4 show the surface pH values corrected for the observed surface temperature. An independent study on the reproducibility of the pH measurements in replicate samples gave a relative standard deviation of ± 0.01 unit.

From Oregon to Hawaii, in series "A", pH tends to increase, from 8.15 to 8.26, toward low latitude. In series "B", from Hawaii to the Aleutians, the surface pH may be expressed by

three values. From $22^{\circ} 50'$ to 35° N an average pH value was 8.23, from 35° to 44° N it was 8.26, and from 44° to 52° N, 8.19. The first transition zone, around 35° N, was very mild, while the second transition at the Subarctic Boundary zone was quite sharp.

DISCUSSION

The general tendency of the pH increase from Oregon to Hawaii is expected from the consideration of increase in water temperature under a constant partial pressure of carbon dioxide in the atmosphere. However, along the Hawaii to Aleutian line a similar temperature dependency is not observed. Within the Central Pacific Water a slight pH increase was observed with the

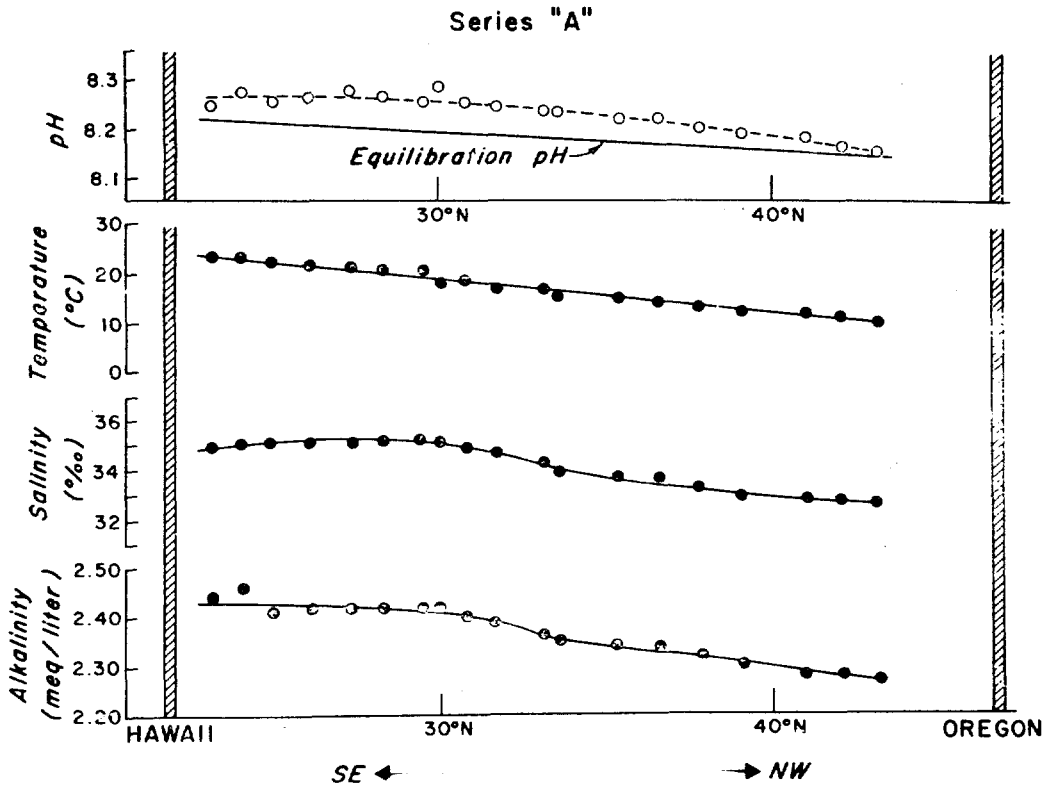


↑ Figure 2. The pH measuring device.

increase in latitude, rather than the expected pH decrease. The sharp pH drop of 0.07 across the Subarctic Boundary zone is quite striking, for the surface temperature decreases gradually across the boundary. Furthermore, the changes in salinity and alkalinity across the boundary cannot produce such a drastic change. It appears that the high pH of 8.26 in Central Pacific Water is inherent to the water mass at this time of the year (June). A brief discussion on the effect of various oceanic parameters on surface pH is given below.

The surface equilibrium pH is a function of temperature, salinity, alkalinity, and partial

Figure 3. Surface pH, temperature, salinity and alkalinity along the Oregon-Hawaii line, series "A". Equilibration pH, with respect to the atmospheric carbon dioxide, is shown along the surface pH values.



Series "B"

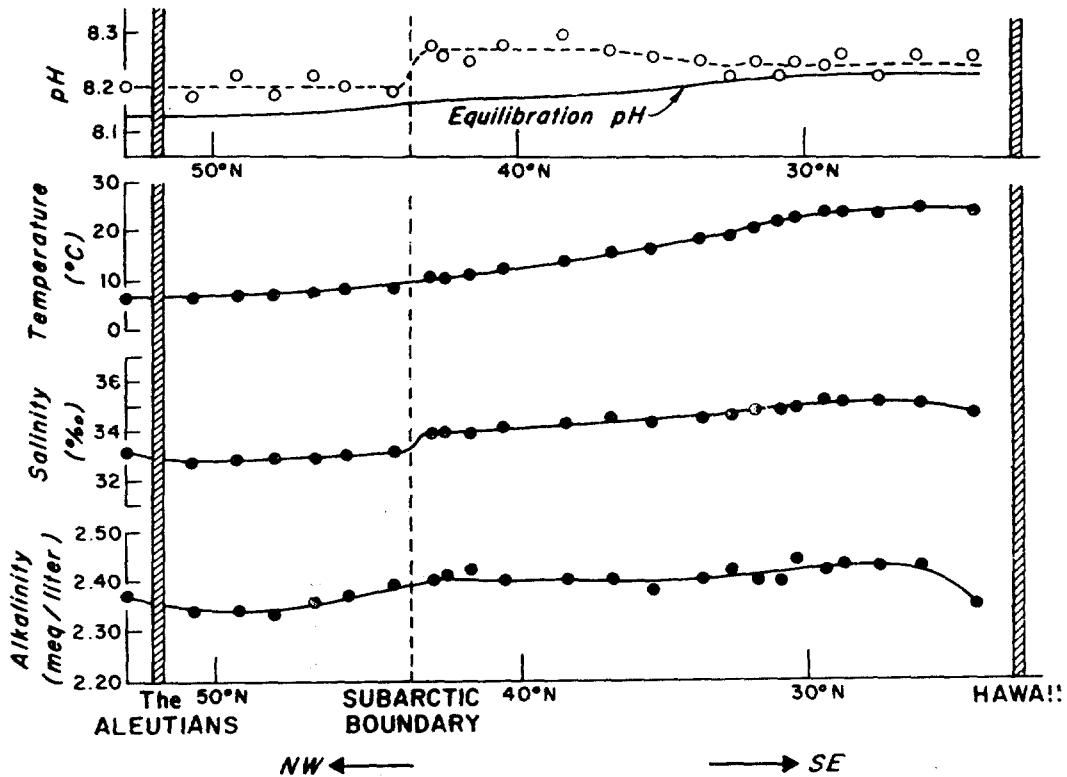


Figure 4. Surface pH , temperature, salinity and alkalinity along the Hawaii-Aleutians line, Series "B". Equilibration pH , with respect to the atmospheric carbon dioxide, is shown along the surface pH values.

pressure of carbon dioxide in the atmosphere immediately above the sea surface. Harvey (1960, p. 172) gives an equation:

$$P_{CO_2} = (\text{Carbonate alkalinity}) \frac{A_{H^+}}{K'_1 \alpha_0 \left(1 + \frac{2K'_2}{A_{H^+}}\right) A_{H_2O}} \quad (1)$$

where P_{CO_2} is the partial pressure of carbon dioxide in the atmosphere, A_{H^+} the hydrogen ion activity, K'_1 and K'_2 the first and second apparent dissociation constants of carbonic acid, α_0 solubility of carbon dioxide in pure water, A_{H_2O} the activity of water in seawater. Carbonate alkalinity is defined as:

$$\text{Carbonate alkalinity} = \text{Alkalinity} - (C_{H_2BO_3^-}) - (CO_3^{2-}) + (C_{H^+}) \quad (2)$$

where C denotes the stoichiometric concentration. Empirically, $C_{H_2BO_3^-}$ is expressed as a function of pH , salinity, and temperature (Harvey 1960, pp. 164-165).

In order to obtain an equation for pH , equation (1) is solved for A_{H^+} :

$$A_{H^+} = 2 \frac{P_{CO_2} \cdot \alpha_0 \cdot A_{H_2O}}{\text{Carbonate alkalinity}} \left[K'_1 + \sqrt{(K'_1)^2 + 8 \frac{\text{Carbonate alkalinity}}{P_{CO_2} \cdot \alpha_0 \cdot A_{H_2O}} K'_1 K'_2} \right] \quad (3)$$

Since $pH = -\log A_{H^+}$,

$$pH = -\log \left\{ 2 \frac{P_{CO_2} \cdot \alpha_0 \cdot A_{H_2O}}{\text{Carbonate alkalinity}} \left[K'_1 + \sqrt{(K'_1)^2 + 8 \frac{\text{Carbonate alkalinity}}{P_{CO_2} \cdot \alpha_0 \cdot A_{H_2O}} K'_1 K'_2} \right] \right\} \quad (4)$$

Carbonate alkalinity is obtainable from the measured alkalinity and a table provided by Harvey (1960, pp. 164-165). The remaining items in equation (4), except P_{CO_2} , are expressed as functions of temperature and salinity. The term α_0 is found in Table 23 of Harvey's book (1960, p. 168) and A_{H_2O} in Table 24 of the same book (p. 169). Lyman (1956) gives tables for the apparent dissociation constants of carbonic acid in seawater, K'_1 and K'_2 .

We assumed that Lyman's constants in equation (4) are valid for working purposes, although his definition of the first apparent dissociation constant is slightly different from that of Buch (cited in Harvey 1960, p. 167):

$$\text{Buch's definition } K'_1 = \frac{(A_{H^+})(A_{HCO_3^-})}{(A_{H_2CO_3})} \quad (5)$$

$$\text{Lyman's definition } K'_1 = \frac{(A_{H^+})(A_{HCO_3^-})}{(C_{CO_2} + C_{H_2CO_3})} \quad (6)$$

where A denotes active concentration or activity. The difference between these two sets of the constants is small. It is 6% at 10°C and 1% at 20°C. Furthermore, we do not have the solubility data of carbon dioxide measured directly in seawater at present, which leads us to use its solubility in pure water assuming $A_{H_2CO_3}$ can be expressed as:

$$A_{H_2CO_3} = (A_{CO_2})(A_{H_2O}) = P_{CO_2} \cdot \alpha_0 \cdot A_{H_2O} \quad (7)$$

Equation (7) is used in equation (4).

The partial pressure of carbon dioxide in the atmosphere over the ocean was not well known until C. D. Keeling of Scripps Institution of Oceanography spearheaded an infrared carbon dioxide analysis beginning the International Geophysical Year of 1957. Recently, Pales, and Keeling (1965) gave a twelve-month running mean carbon dioxide concentration at Mauna Loa Observatory (Hawaii) for June 1963 as 317 ppm. They also indicated that an annual rate of increase of carbon dioxide was 0.68 ppm/year during 1959-1963. If the same rate of

increase has existed during 1963-1966, then the mean carbon dioxide concentration for April-June 1966 would be about 319 ppm. We used this extrapolated value of 319 ppm to calculate the equilibrium pH in the surface water.

Calculated values of carbonate alkalinity had a small range of 2.19 to 2.33 meq/liter. A_{H_2O} in the salinity range of 32.7 to 35.2 ‰ was 0.982 to 0.981. Therefore, it can be taken as a constant of 0.982. α_0 in the temperature range of 6.6° to 25°C varied from 0.0607 to 0.0342 mole/liter. Hence, it is a strong function of temperature. K'_1 and K'_2 vary greatly with temperature, but little with salinity. K'_1 had a range of 0.79×10^{-6} at 6.6°C and 33.2‰ S to 1.02×10^{-6} at 25.0°C and 35.1‰ S, while K'_2 changed from 0.47×10^{-9} to 1.04×10^{-9} respectively. When we summarize the above ranges and dependency for the items in equation (4), it is obvious that the surface pH in seawater is affected strongly by temperature and weakly by alkalinity, salinity, and partial pressure of carbon dioxide. Table 1 clearly shows the strong temperature dependency of the surface equilibrium pH over other variables. In general, the equilibration pH is lower than the measured data. If we assume that all the values and constants used in the equation (4) are valid, then we see that the ocean we studied is undersaturated with respect to the atmospheric carbon dioxide. Consequently, carbon dioxide should enter into the ocean from the atmosphere. Qualitatively, the undersaturation of carbon dioxide is the strongest immediately south of the Subarctic Boundary zone (Fig. 4). Our qualitative statement of the undersaturation agrees fairly well with Postma's (1964) tentative geographical pattern of exchange of carbon dioxide between the Pacific Ocean and the atmosphere. One exception is that near the Aleutian Islands we do not find the oversaturation of carbon dioxide Postma gave. This disagreement may be

attributed simply to the different seasons, different years of water sampling, as well as to uncertain-

ty of the numerical values used in equation (4).

Table 1. Effect of various parameters on the surface equilibration pH of a hypothetical seawater.

	Equilibration pH	ΔpH
At 10° C, 33‰ S, 319 ppm P_{CO_2} 2.20 meq/liter carbonate alkalinity	8.14	—
If only <i>temperature</i> is changed to 20° C	8.20	0.06
If only <i>salinity</i> is changed to 35‰ S	8.13	-0.01
If only P_{CO_2} is changed to 326 ppm (comparable to a 10-year change)	8.13	-0.01
If only <i>carbonate alkalinity</i> is changed to 2.30 meq/liter (comparable to $CaCO_3$ dissolution of 5 mg/liter)	8.16	0.02

The cause of the existence of nonequilibrium pH , especially near the Subarctic Boundary zone, is not clear. It may be biological (organic) or physical in origin.

In summary, the surface pH of the Northeastern Pacific Ocean does not appear to be in equilibrium with atmospheric carbon dioxide. Generally, the surface pH is lower than the equilibration pH . During April-June 1966, the surface water appears to be undersaturated with respect to carbon dioxide in the atmosphere. In order to obtain a reliable equilibrium pH , a direct measurement of the solubility of carbon dioxide in seawater is needed.

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